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**Synthesis of Oligomers / Polymers from Plant Oil Derivatives**

**By**

**Seng Soi Hoong**

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in Chemistry

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## **Declaration**

The work presented in this thesis is the original work of the author. References to previous related results and ideas have been fully acknowledged. All work was performed in the Department of Chemistry at the University of Warwick between April 2009 and April 2012 and has not been submitted for a degree at any other institution.

Seng Soi Hoong

## **Abstract**

The work presented in this thesis represents the chemical modifications of unsaturated plant oils to yield oligomeric/polymeric polyols suitable for polyurethane synthesis. Chapter 1 provides the introduction to the chemistry of polyurethanes, plant oils and plant oil based polyols. Chapter 2 focus on making oligomeric polyols from unsaturated plant oils through epoxidation and subsequent epoxide ring opening oligomerization that yielded oligomeric polyols. The properties of these oligomeric polyols were influence by the level of unsaturation of the plant oils. In addition, catalyst loading, monomer concentration and reaction time play vital role in determining the properties of the oligomeric polyols. Plant oil based polyols were also prepared by epoxide ring opening with renewable polyhydric alcohols that provide a variety of plant oil based polyols for polyurethane synthesis.

Chapter 3 focus on the synthesis of polyurethanes (PU) from various types of plant oil based polyols as well as the evaluation of the mechanical properties of these synthesized PU. The tensile test of the PU shows that the mechanical properties were related to the structure and functionalities of the plant oil based polyols. The bulk of Chapter 4 discusses the copolymerization of epoxidized plant oils with tetrahydrofuran and the use of these copolymers for the synthesis of PU. The properties of the copolymers were related to the epoxidized oils used in the reaction and therefore influence the mechanical properties of the PU synthesized from them. Finally, Chapter 5 is a collection of work on the one-pot oligomerization of unsaturated fatty acid and plant oils with and without catalyst as well as the synthesis of PU based on these polyols.



## Abbreviations

AV	Acid value
COSY	H-H correlation spectroscopy
d	doublet
dd	doublet of doublets
Da	Dalton
DCM	Dichloromethane
DSC	Differential scanning calorimetry
ECB	Epoxidized cocoa butter
EuO	Euphorbia oil
EMO	Epoxidized methyl oleate
EO	Ethylene oxide
EPO	Epoxidized palm oil
ERO	Epoxidized rapeseed oil
ESO	Epoxidized soybean oil
ESI	Electrospray ionization
FAC	Fatty acid composition
GPC	Gel permeation chromatography
<i>HP</i>	Hydroxylated plant oil polyols
HRMS	High resolution mass spectrometry
IR	Infra-red
m	multiplet
MALDI-TOF-MS	Matrix-assisted laser desorption/ionization time of flight mass spectrometry
MDI	4,4'-methylene diphenyl diisocyanate
$M_n$	Number average molecular weight
mol eq	mol equivalent
MPa	Megapascal
mW	miliWatt
$M_w$	Weight average molecular weight
NCO	Isocyanate group
NMR	Nuclear magnetic resonance
OH	Hydroxyl group

OHV	Hydroxyl value
OOC	Oxirane oxygen content
OP	Oligomeric polyols
PDI	Polydispersity index
PEG600	Polyethylene oxide, average molecular weight of 600 Da
PEG3350	Polyethylene oxide, average molecular weight of 3350 Da
ppm	Parts per million
PO	Propylene oxide
POP	Plant oil based polyols
PPT	Phosphotungstate catalyst system
PTC	Phase transfer catalyst
PTHF-EO/PO	Copolymers of PTHF with EO or PO
PTHF	Polytetrahydrofuran
<i>p</i> -TSA	<i>para</i> toluene sulfonic acid
PU	Polyurethane
s	singlet
t	triplet
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
TP	Tungsten powder catalyst system

## CHAPTER 1 - INTRODUCTION

### 1.1 POLYURETHANE

The polyurethanes (PU) are polymers that contain significant amount of the urethane group (Figure 1.1) as a repeating structural unit in the polymer chain.

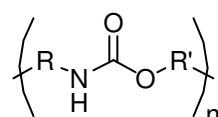


Figure 1.1 Structural unit of urethane

The urethane group  $\text{-NH-COO-}$  can be considered as an ester of the hypothetically unstable carbamic acid or an amide ester of carbonic acid.<sup>1</sup> The first reported synthesis of a urethane compound was ethyl carbamate by Wurtz in 1849, where he reacted ethyl isocyanate with ethyl alcohol to give the urethane compound.<sup>2</sup>

There are various methods<sup>3</sup> to synthesize the urethane group but the most commercially important method is the reaction between an alcohol and an isocyanate.<sup>4</sup> This commercially important reaction was investigated intensively by Dr. Otto Bayer and co-workers in 1937 to synthesize the first polyurethane<sup>5</sup> as a response to the commercially successful nylon fibers by Carothers. In addition, they also discovered a new type of polymerization reaction, namely the polyaddition reaction,<sup>6</sup> which is similar to the classical polycondensation reaction but without the formation of by-product.

Since its discovery in 1937, PU has found applications in many aspects of our daily life. The production of PU materials in Asia-Pacific alone in 2009 was estimated to

be about 7 million tonnes. The following shows the main applications of PU products in Asia-Pacific in 2009 according to product sector, (Figure 1.2).<sup>7</sup>

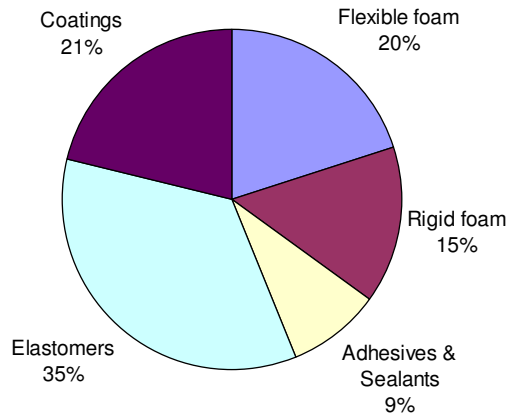


Figure 1.2 PU applications according to product sector

The capability of PU polymers to fulfill various application requirements comes from the fact that they can be produced with a wide range of properties that can be linked to the structure of the PU in terms of crosslink densities<sup>8</sup> and stiffnesses, (Figure 1.3).

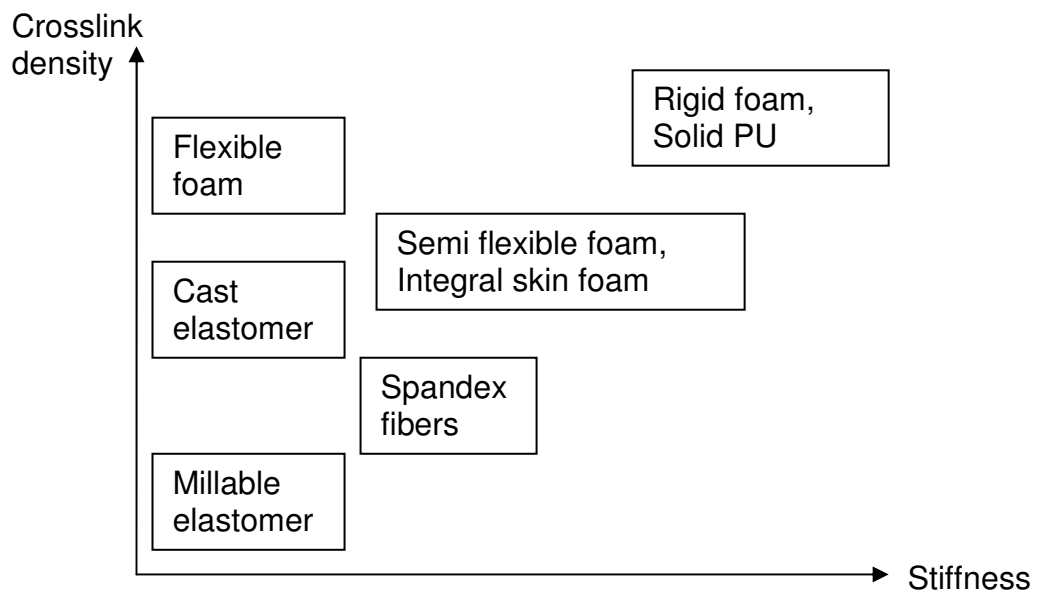


Figure 1.3 PU classified by crosslink density and stiffness

The structure of the PU polymer determines the mechanical and thermal properties of PU products. The structure of a PU on a microscopic level can be divided into two segments. One of the segments is known as the ‘hard/rigid’ segment and the other segment is known as the ‘soft/flexible’ segment. The hard segment is formed by the urethane and urea linkages in the PU, while the soft segment is made up of polyol chain<sup>9</sup> (Figure 1.4).

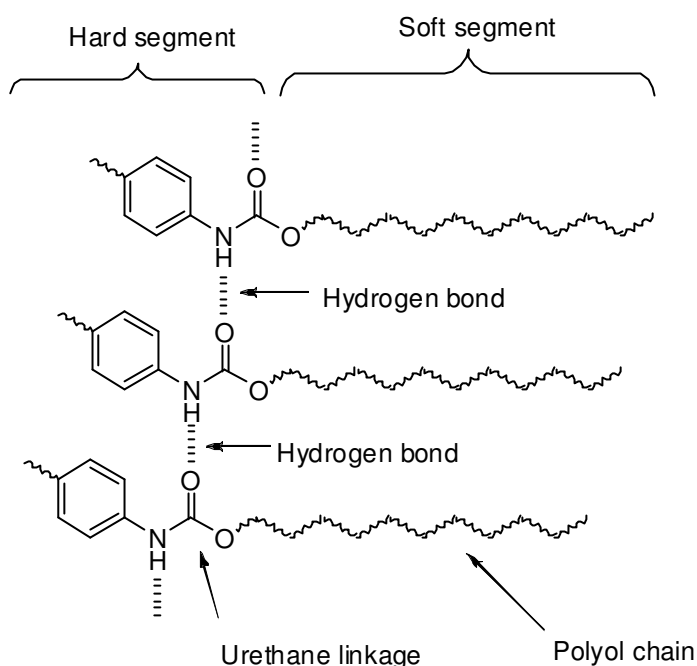


Figure 1.4 Hard segment and soft segment in PU

It is the soft segment (polyol derived) of the PU that imparts the flexible properties to the material. Generally, there are two types of polyols available commercially in the PU industry. The first type of polyol has high molecular weight in range of 2,000-10,000 dalton (Da) and low functionality in the range of 2-3 hydroxyl groups per mol. This type of polyol is used in making flexible PU. Meanwhile, the second type of polyol has low molecular weight in the range of 300-1000 Da and higher

functionality in the range of 3-8 hydroxyl groups per mol and this type of polyol is more suitable for making rigid PU.<sup>10</sup>

Thermoplastic PU structures can be made from the reaction between diisocyanates and high molecular weight polyols (3000 Da) which have a hydroxyl functionality of 2 per mol. The high molecular weight of the polyol assures high mobility of the polymer chain and therefore gives rise to high elasticity of the PU.

The urethane and urea functional groups in the thermoplastic PU (hard segment) can form hydrogen bonds and this promotes association between the urethane/urea linkages, (Figure 1.5). The incompatibility between the soft and hard segments also contributes to the formation of this higher ordered structure.<sup>11</sup>

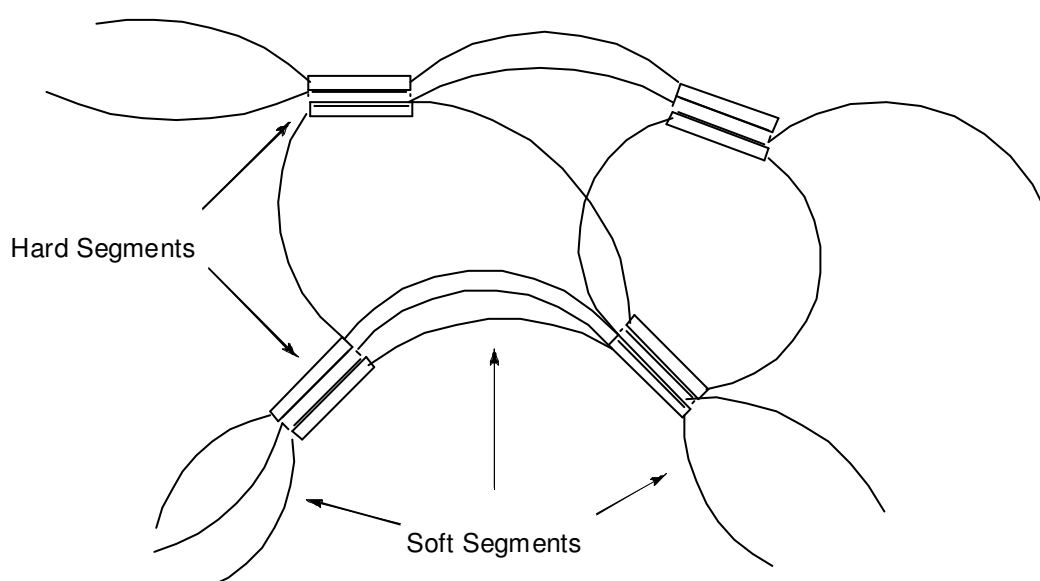


Figure 1.5 Hard segments and soft segments of thermoplastic PU

The hard segments provide a physical crosslinked structure to the thermoplastic PU by hydrogen bonding. When the thermoplastic PU is heated to a high enough temperature, the hydrogen bonds that hold the hard segments together can be broken

and the PU polymer chains are able to move freely. This enables the thermoplastic PU to be processed into any shape by ‘melting’.<sup>12</sup>

Flexible PU structures can be made from polyols that have low hydroxyl functionality (about 2-3 hydroxyl groups per mol) and high molecular weights (about 3000-6000 Da). When reacted with a diisocyanate, this polyol type will yield flexible PU with low crosslinked densities<sup>13</sup> which can be hypothetically illustrated in Figure 1.6. The long polymer chains of the high molecular weight polyol will impart flexibility to the PU structure.

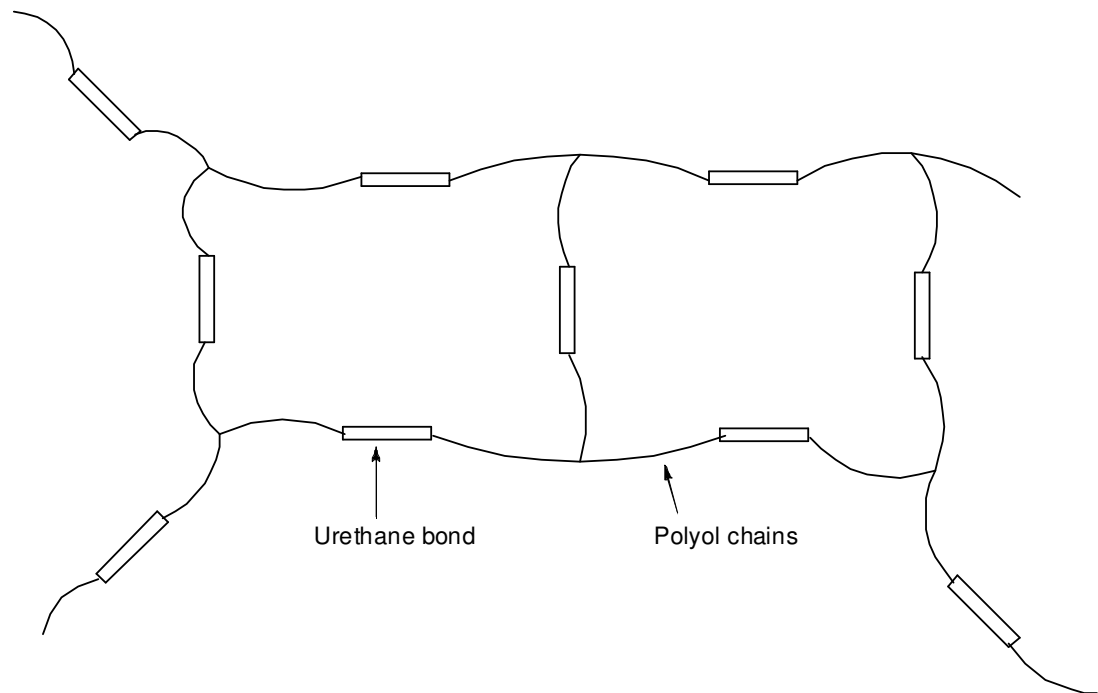


Figure 1.6 Hypothetical morphology of flexible PU structure

Rigid PU structures are usually made from polyols that have high hydroxyl functionality (about 3-8 hydroxyl groups per mol) and low molecular weights (about 300-1000 Da). The high functionality of the polyol ensures that when it is reacted with diisocyanates or polyisocyanates (having 2-4 NCO group per mol), the resulting

PU has a high crosslink density and the high rigidity. Furthermore, the relatively short polymer chains of the low molecular weight polyol monomer do not allow the rigid PU to move freely and therefore, impart rigidity to the PU structure.<sup>14</sup> The hypothetical structure of the rigid PU can be illustrated in Figure 1.7.

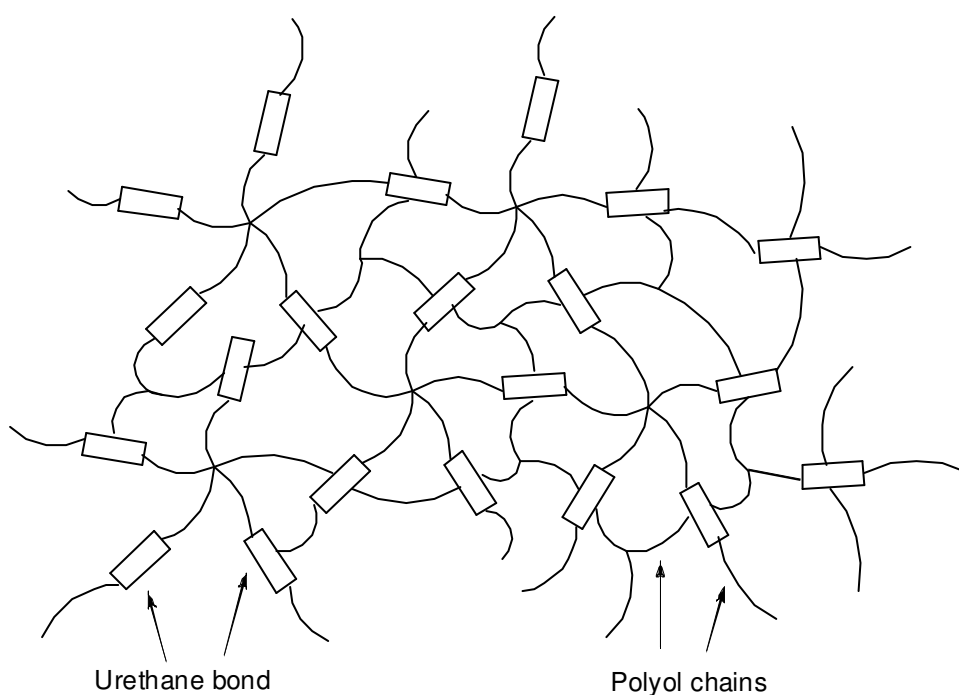


Figure 1.7 Hypothetical structure of rigid PU

In order to fully understand the formation of these different types of PU structures (thermoplastic, flexible and rigid), the following sections will dwell on the building blocks of the PU, namely the isocyanates and polyols by looking at different types of diisocyanates and polyols as well as the chemistry aspect of diisocyanates and polyol.



## 1.2 DIISOCYANATE

All commercially available diisocyanates are prepared through phosgenation of their respective primary amines. These diisocyanates can be divided into two groups, namely aromatics and aliphatics. Examples of aromatic diisocyanates are 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate (MDI). Aliphatic diisocyanates commonly use commercially are 1,6-hexamethylene diisocyanate and isophorone diisocyanate.<sup>15</sup> The structures of these diisocyanates are given in Figure 1.8.

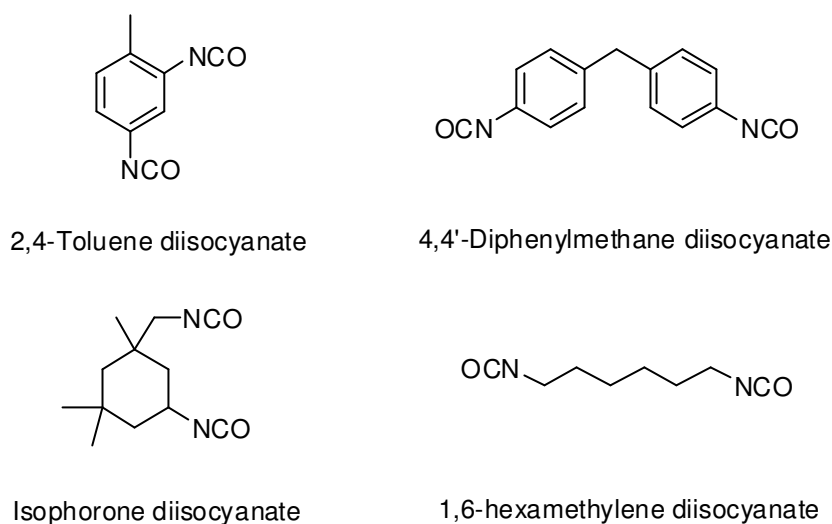


Figure 1.8 Aromatic and aliphatic diisocyanates.

Generally, aromatic diisocyanates are preferred over aliphatic ones because the aromatic diisocyanates have much higher reactivities than aliphatic diisocyanates in the PU reaction.<sup>15</sup> In addition, the aromatic diisocyanates are relatively cheap to produce as compared to the aliphatic feedstocks. However, the aliphatic diisocyanates have better light stability properties compared to aromatic diisocyanate, where the aromatic diisocyanates tend to yellow very quickly under sunlight.

Therefore, the aliphatic diisocyanates are usually used in applications where light stability is a required property.<sup>16</sup>

### 1.2.1 REACTION OF ISOCYANATE WITH ALCOHOL

The reaction between the NCO and alcohols is the most familiar of all the reaction of isocyanates. Nearly all commercial applications of the NCO functional group, such as foams, elastomers and coatings are based on this reaction. The reaction of an NCO group with an alcohol functionality gives a urethane functional group, which is also known as the carbamate group<sup>17</sup> (Figure 1.9).



Figure 1.9 Reaction between isocyanate and alcohol

The reaction of an NCO group with simple primary alcohols and secondary alcohols usually give nearly quantitative yields of the urethane. However, there is significant reaction rate difference between primary and secondary alcohols due to the effect of steric hindrance. Consequently, primary alcohols generally react readily at 25 °C, while secondary alcohols typically react at only a third of this rate. The steric hindrance effect is most profound for tertiary alcohols which react much more slowly than primary alcohols, approximately 0.005 as fast as a primary alcohol.<sup>18</sup>

### 1.2.2 REACTION OF ISOCYANATE WITH AMINE

Generally, the reaction between the NCO and an amine is much faster than for an alcohol due to the stronger nucleophilicity of amine group. The reaction between a primary aliphatic amine and an NCO group is 1000 times faster than for a primary aliphatic alcohol. In addition, the secondary aliphatic and primary aromatic amines are 200 and 2 times faster than primary aliphatic alcohols respectively.<sup>19</sup>

Therefore, the primary aliphatic amine is extremely reactive with NCO at 0-25 °C, yielding a disubstituted urea (Figure 1.10). This fast reaction ensures that the curing of polyurea products is not affected by moisture and temperature.<sup>20</sup> Therefore, polyurea coatings are used in areas where the dampness is high and fast curing is required.

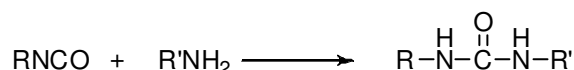


Figure 1.10 Reaction between isocyanate and amine

### 1.2.3 REACTION OF ISOCYANATE WITH CARBOXYLIC ACID

The reaction between a NCO group and a carboxylic acid is much slower than its reaction with amines and alcohols<sup>19</sup> and produces a mixture of unstable anhydrides, which decomposes to yield amides and gaseous carbon dioxide<sup>21</sup> (Figure 1.11).

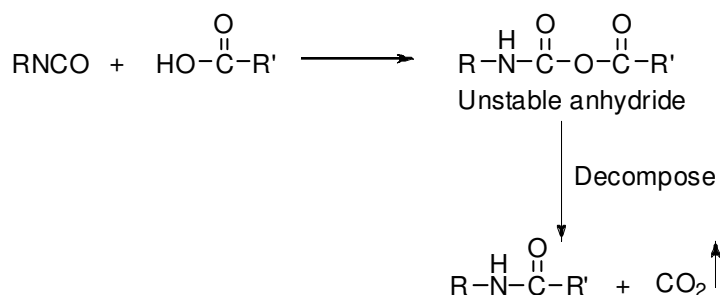


Figure 1.11 Reaction of isocyanate with carboxylic acid

A study has been conducted with  $^{14}\text{C}$  labelled carboxylic acids to find out the carbon source of the gaseous carbon dioxide evolved from the reaction. The analysis results revealed that the carbon source comes from the isocyanate.<sup>22</sup>

### 1.3 POLYOL

There are two categories of polyols used in the production of PU products. The first category is the low molecular weight molecules with well defined molecular weight such as 1,4-butanediol, diethylene glycol and glycerol. These polyols are currently used in the PU industry as chain extenders or crosslinkers, depending whether they are a diol or triol.<sup>8</sup>

The second category is polyols with relatively high molecular weight (oligo-polyol) (300-10000 Da) that is having a molecular weight distribution characterized by an average molecular weight. These polyols have primary or secondary hydroxyl functionality of 2-8 per mol. Generally, there are two types of commercially available oligo-polyols based on the functional group of the repeating unit, namely the polyethers and the polyesters.<sup>1</sup>

### 1.3.1 POLYETHER POLYOL BY ANIONIC POLYMERIZATION

Polyether polyols based on alkylene oxide are the most commercially important polyol, which represents about 53% of the total polyol production in Asia Pacific in year 2009.<sup>7</sup> The common alkylene oxides used in making polyether polyols are ethylene oxide (EO), propylene oxide (PO) and butylene oxide<sup>23</sup> (Figure 1.12). The general structure of the polyether polyols derived from polymerization of alkylene oxide is illustrated in Figure 1.12.

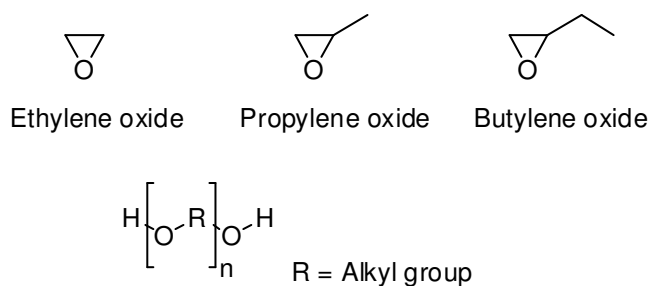


Figure 1.12 Alkylene oxides and general structure of polyether polyol

The polymerization of alkylene oxides is initiated by chain initiators that contain active hydrogen atoms such as the hydroxyl group. Depending on the desired final functionality of the polyether polyol, the chain initiator can be selected from compounds having 2-6 hydroxyl functionalities, in which the same number of functionalities will be transferred to the polyether polyol. Example of chain initiators that have been used in industry are diethylene glycol, glycerol, trimethylolpropane, pentaerythritol and sucrose<sup>1</sup> (Figure 1.13).

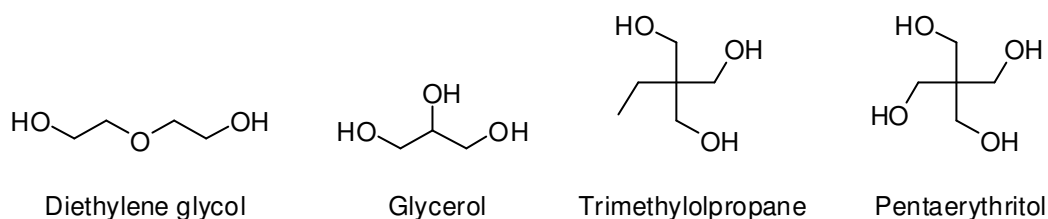


Figure 1.13 Chain initiators used in polymerization of alkylene oxide

The alkylene oxide polymerization reaction is usually catalyzed by one of the three types of catalysts, namely anionic, cationic and coordinative catalysts. Examples of compounds used as anionic catalyst are hydroxide of alkaline metal (NaOH, KOH), calcium naphthenates and calcium octanoates.<sup>24</sup>

The cationic catalysts used in the polymerization are Lewis acids and Bronsted acids ( $\text{SbF}_5$ ,  $\text{BF}_3$ ,  $\text{HSbF}_6$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ).<sup>25</sup> Meanwhile, examples of the coordinative catalysts used in the polymerization are zinc and titanium alcoholates [ $\text{Zn}(\text{OR})_2$ ,  $\text{Ti}(\text{OR})_4$ ], zinc and aluminum tetraphenyl porphyrans.<sup>26</sup> However, the two most important catalysts used for the synthesis of high molecular weight polyether polyols on industrial scales are potassium hydroxide and the double metal cyanide catalyst  $\text{Zn}_3[\text{Co}(\text{CN})_6]_3 \cdot \text{ZnCl}_2$  with various ligands.<sup>27</sup>

The most important polyether polyols are the polyether triols because they are used in the biggest sector of PU industry namely that of flexible PU foam. The polyether triols are made from random copolymerization of propylene oxide and ethylene oxide initiated by glycerol<sup>28</sup>, with an average molecular weight of 3000-3600 Da.

The first step in the production of a polyether triol is the formation of potassium glycerolate and water from the equilibrium reaction between glycerol and potassium hydroxide (Figure 1.14). In order to shift the equilibrium to the formation of potassium glycerolate, the water of reaction is removed under vacuum at 100-130 °C.

In the end, a solution of potassium glycerolate in glycerol is formed, which is known as the initiator solution. The next step of the production of polyether triol involved the slow addition of the propylene oxide/ ethylene oxide mixture to the initiator solution at 115 °C and 2-5 bar pressure.<sup>29</sup>

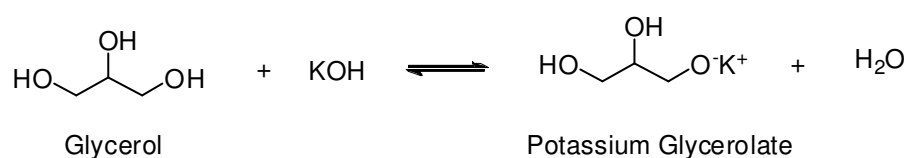


Figure 1.14 Reaction between potassium hydroxide and glycerol

The reaction between potassium glycerolate and propylene oxide is a S<sub>N</sub>2 nucleophilic substitution reaction, in which the strong nucleophile alcoholate group attacks the carbon atom of the alkylene oxide, causing ring opening of the oxirane group<sup>30</sup> (Figure 1.15).

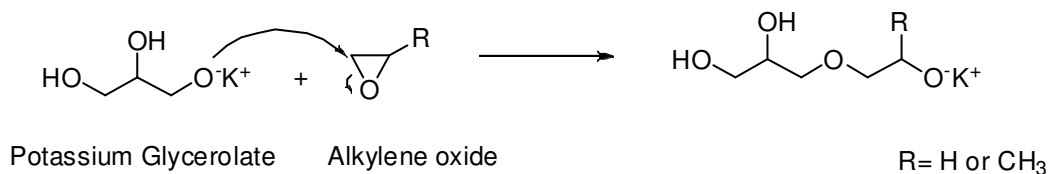


Figure 1.15 S<sub>N</sub>2 nucleophilic reaction between potassium glycerolate and alkylene oxide

Referring to Figure 1.15, the product of this reaction is another alcoholate group, which can attack the oxirane ring of another alkylene oxide and this extends the molecule with another unit of alkylene oxide (Figure 1.16). This process repeats until the alkylene oxide is fully consumed. The final step of the process is the neutralization of the product (polyether polyol) with inorganic acids and removal of the salts.<sup>30</sup>

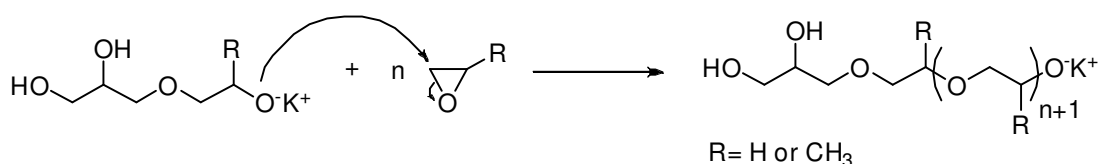


Figure 1.16 Polymerization of alkylene oxide

### 1.3.2 POLYETHER POLYOL BY CATIONIC POLYMERISATION

The cationic polymerization method is used to produce polyether polyols from homopolymerization of tetrahydrofuran (PTHF) and copolymerization of tetrahydrofuran with ethylene oxide or propylene oxide (PTHF-EO/PO). However, only the cationic homopolymerization of tetrahydrofuran is commercially important due to its application in the production of PU elastomers and elastic fibers (Spandex fibers). In addition, the higher cost of tetrahydrofuran also restricts the use of PTHF and PTHF-EO/PO polyols in the flexible PU foams area.<sup>31</sup>

The ring opening homopolymerisation of tetrahydrofuran is conducted at 0-30 °C in the presence of Lewis acids or Bronsted superacids such as  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ ,



fluorosulfonic acid, triflic acid and triflic anhydride.<sup>32</sup> An example of the initiation step of the polymerization reaction is illustrated in Figure 1.17, in which the homopolymerization of tetrahydrofuran is initiated by propionyl chloride and catalyzed by AgSbF<sub>6</sub>. The reaction between the propionyl chloride and the catalyst generates the oxocarbenium salt, which is the active catalyst species.<sup>33</sup>

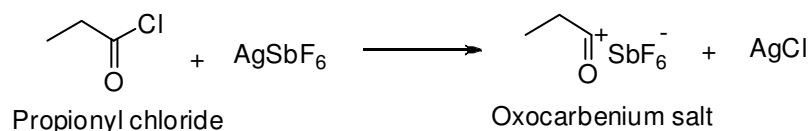


Figure 1,17 Formation of oxocarbenium salt.

The next step in the polymerization process is the propagation step where the oxocarbenium salt reacts with tetrahydrofuran (THF) to form the activated chain end species and this reaction is repeated with more THF molecule to form the polyether polyol based on THF. The termination step of the polymerization reaction is conducted with water to yield a terminal hydroxyl group (Figure 1.18). Finally, the polyether polyol is subjected to hydrolysis reaction in order to remove the propionyl group and yield telechelic polyether polyol.<sup>33</sup> The polyether polyol based on homopolymerization of THF usually has an average molecular weight of 650-2000 Da.

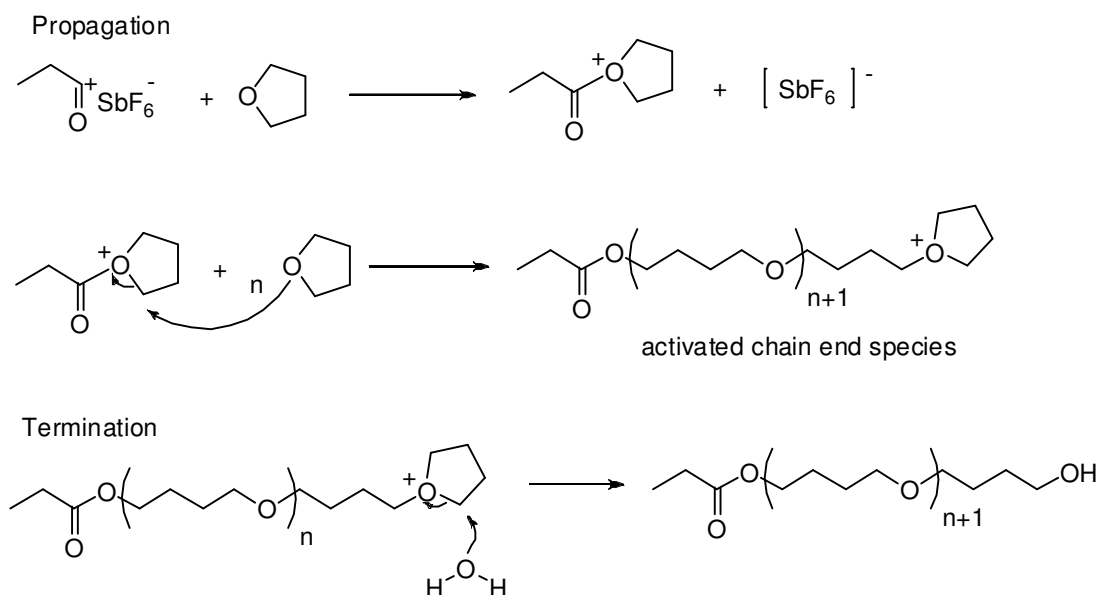


Figure 1.18 Propagation and termination step of THF polymerization

## 1.4 POLYESTER POLYOL

Polyester polyols are the second most important type of oligo-polyol after polyether polyols as raw material for the production of PU's. The polyester polyols represent about 27% of the market in Asia Pacific oligo-polyols in year 2009, which corresponds to about 785,000 tonne. Most of the polyester polyols are used in the production of PU elastomers and coatings.<sup>7</sup>

Polyester polyols for PU application usually have a molecular weight range<sup>34</sup> from 1000-4000 Da. They are characterized by the presence of ester groups as the repeating unit in the polymer and terminal hydroxyl groups. The general formula for the polyester polyol is illustrated in Figure 1.19.

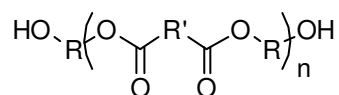


Figure 1.19 General formula for polyester polyol

The conventional method used industrially to produce a polyester polyol is the polycondensation reaction between a glycol (or polyol) and a dicarboxylic acid, in which the by-product of the reaction is water (Figure 1.20).

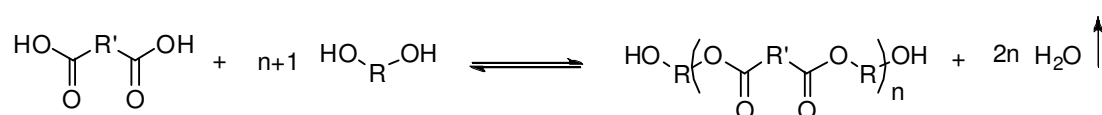


Figure 1.20 Polycondensation reaction between glycols and dicarboxylic acids

This reaction is an equilibrium reaction and the method to shift the equilibrium to the formation of polyester polyol is through continuous removal of water. Therefore, the polycondensation is usually conducted at about 200 °C under continuous reduced pressure to remove water from the reaction. The polycondensation reaction can be catalysed by compounds such as *p*-toluene sulfonic acid, stannous octoate and zinc acetate.<sup>1</sup>

The other method used industrially to produce polyester polyols is the transesterification reaction between dimethyl esters of dicarboxylic acids and glycols, in which alcohol is the by-product of the reaction instead of water. For example, the reaction between 1,4-butanediol and dimethyl adipate with titanium tetrabutoxide [Ti(OBu)<sub>4</sub>] as the catalyst was conducted at 200 °C and yielded polyester polyols with methanol as the by-product<sup>35</sup> (Figure 1.21).

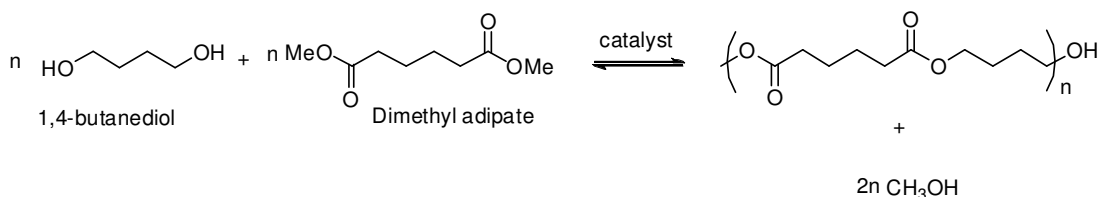


Figure 1.21 Transesterification between 1,4-butanediol and dimethyl adipate

Another method that is used to produce polyester polyols is through ring opening polymerization of cyclic esters. Examples of cyclic esters that can be polymerized to polyester polyols are  $\epsilon$ -caprolactone and  $\delta$ -valerolactone. For example,  $\epsilon$ -caprolactone was polymerized to polyester polyol through ring opening polymerization catalyzed by Sm(II) aryloxide complexes at room temperature<sup>36</sup> (Figure 1.22).

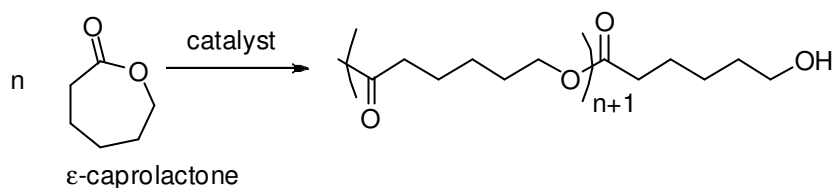


Figure 1.22 Polymerization of  $\epsilon$ -caprolactone.

Initiation of the ring opening polymerization of  $\epsilon$ -caprolactone occurs by activation with a metal catalyst ( $\text{La}(\text{acac})_3$ ,  $\text{Pr}(\text{acac})_3$ ,  $\text{Nd}(\text{acac})_3$ )<sup>37</sup> through the coordination mechanism shown in Figure 1.23. The activated carbonyl group is then attacked by the alcoholate group from the catalyst which causes carbonyl-oxygen bond cleavage and a new activated chain end species with the metal center at the end of the chain<sup>37</sup> (Figure 1.23).

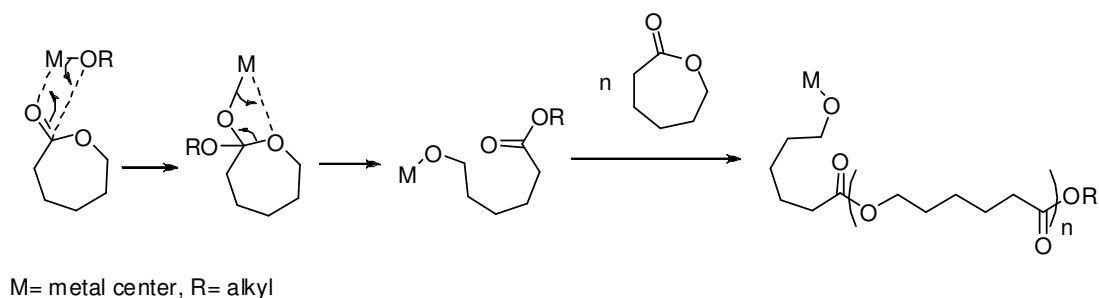


Figure 1.23 Mechanism for polymerization of  $\epsilon$ -caprolactone with metal alkoxide catalyst.

This activated chain end species can repeat the whole process again with more  $\epsilon$ -caprolactone to propagate the polymer chain. The polymerization is terminated by addition of methanol or ethanol to yield a polyester with a terminal hydroxyl group.

## 1.5 RENEWABLES CONTENT IN POLYURETHANE

Currently, most of the PU raw materials (polyols and isocyanates) are derived from the non-renewable petroleum resources, which will be depleted in the future. The scientific community as well as the chemical industry is carrying out research and development to find alternatives to the petrochemicals based raw materials.

Most of the research and development work on renewable PUs have been focusing on renewable polyols and less focus was on diisocyanates. Renewable polyols have been made from bio-based materials such as carbohydrates, lignin and plant oils. This will be discussed in the following section. In contrast, the synthesis of renewable diisocyanates<sup>43,44,45</sup> has been made only from plant oils.

Plant sugars such as glucose, xylitol and sorbitol (Figure 1.24), which have multiple hydroxyl groups, have been used as initiators for the production of polyether polyols, where the plant sugars were reacted with propylene oxide or ethylene oxide in the presence of KOH as the catalyst.<sup>38</sup> Polyesters were also be produced from glucose when it was reacted with  $\epsilon$ -caprolactone and ethylene glycol at 150 °C with tin (II) 2-ethylhexanoate as the catalyst.<sup>39</sup>

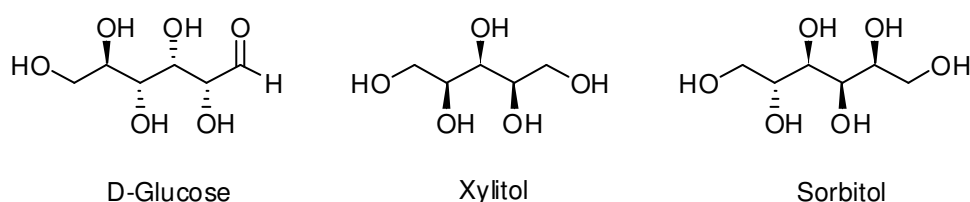


Figure 1.24. Example of plant sugars used as initiator in polyols production

Lignin is basically an aromatic based macromolecular compound that has primary and secondary hydroxyl group<sup>40</sup> (Figure 1.25). Lignin recovered from the paper pulping process was used as starting material to make PUs by dissolving it in an ethylene oxide based polyether polyol and reacting the mixture with a diisocyanate to yield rigid PU.<sup>41</sup>

Lignin based polyester polyols were produced by reacting the lignin with a dibasic acid and diethylene glycol. The resulting polyester polyol had a hydroxyl value of 305 mg KOH/g sample and it was used to make rigid PU.<sup>42</sup>

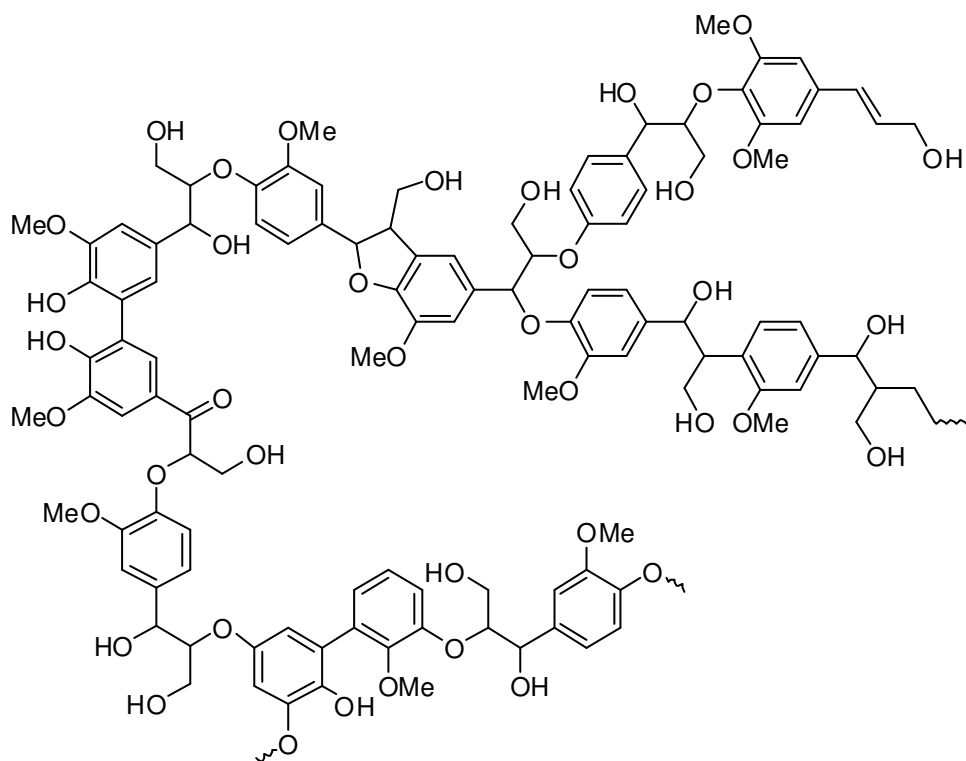


Figure 1.25 Idealized structure of lignin

Plant oils are the main source of renewable material used in the synthesis of both renewable polyols (see Section 1.7) and renewable diisocyanates. Three examples of natural oil based diisocyanate synthesis have been reported.<sup>43,44,45</sup> In one of the examples (Figure 1.26), oleic acid (**1.1**) was subjected to ozonolysis to yield the aldehyde compound (**1.2**). This aldehyde was then oxidized with *tert*-butyl hydroperoxide to yield (**1.3**). Then (**1.3**) was reacted further with sodium azide to give an intermediate which then underwent a Curtius rearrangement to yield (**1.4**).<sup>43</sup>

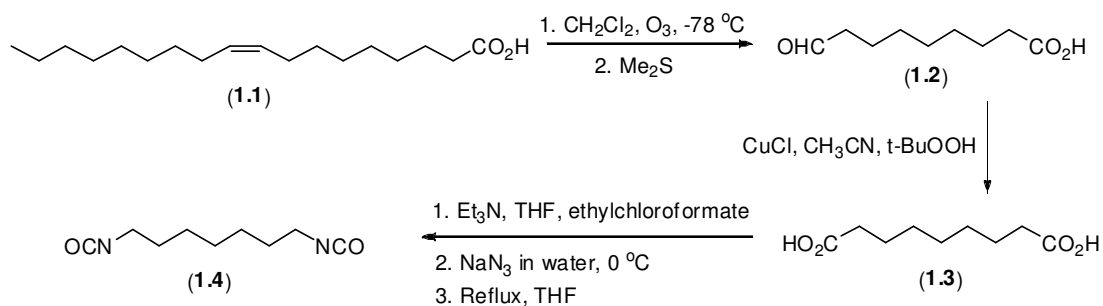


Figure 1.26 Synthesis of **(1.4)** from **(1.1)**

In another example (Figure 1.27), the first step of the synthesis utilized a self-metathesis reaction of **(1.1)** to yield a diacid **(1.5a)** which again was treated with sodium azide to yield the target diisocyanate **(1.6)** via a Curtius rearrangement.<sup>44</sup> The co-product from this reaction was a long chain alkene **(1.5b)**.

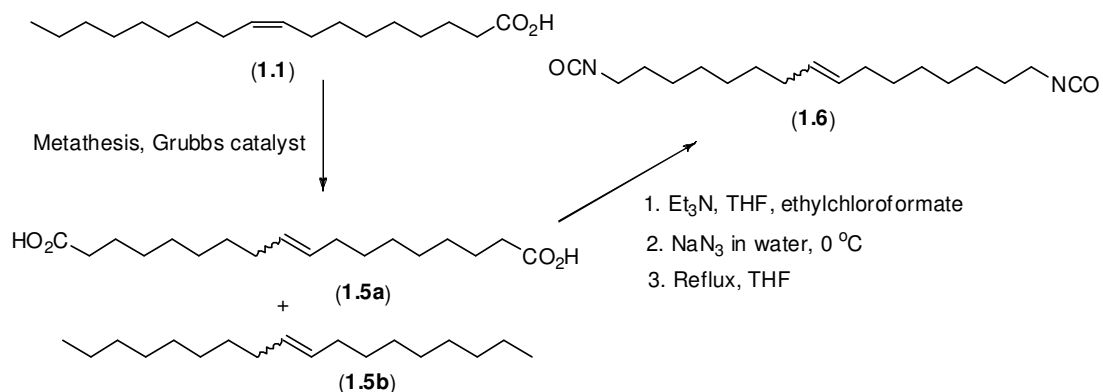


Figure 1.27 Synthesis of **(1.6)** from **(1.1)**

A conceptually different approach (Figure 1.28) utilized an allylic bromination of **(1.7)** as the first step to yield **(1.8)**. Then **(1.8)** was reacted with  $\text{AgNCO}$  to prepare the target isocyanate functionalized **(1.9)**.<sup>45</sup>



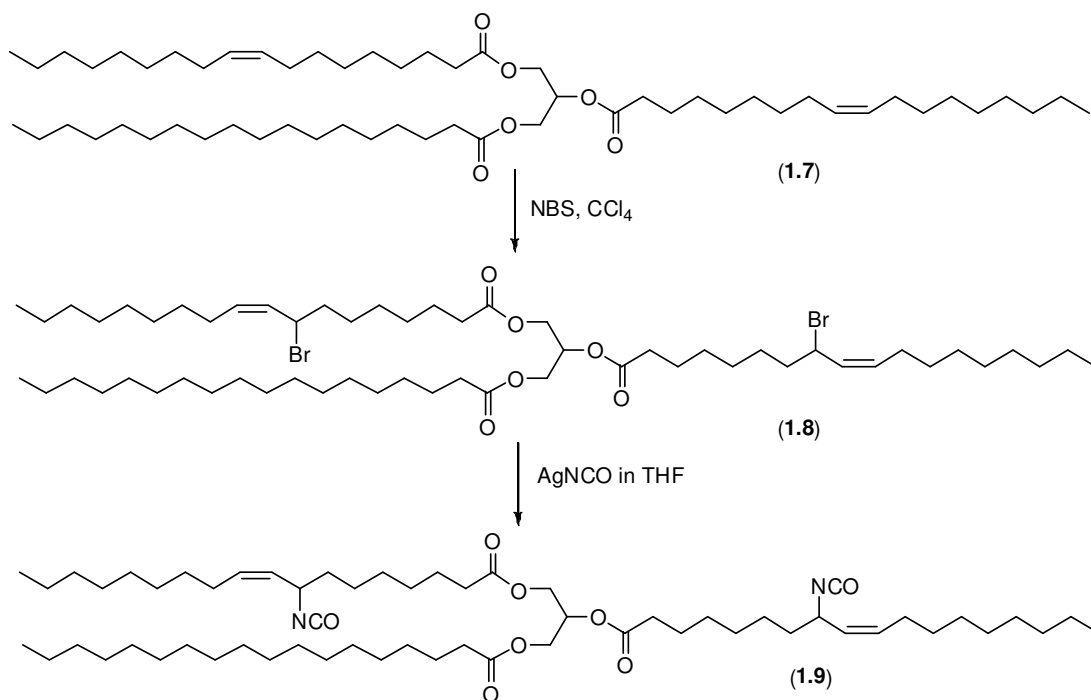


Figure 1.28 Synthesis of plant oil based diisocyanate

The importance of plant oils as a raw material to produce renewable polyols will be better understood after detail discussion on the chemical composition and chemistry of plant oils in the following section.

## 1.6 PLANT OIL

The global production of oils and fats in 2010/11 was about 150 million tonnes. Most of the oils and fats were consumed as food, which is about 80% of the total volume, while the rest was used for non-food uses such as oleochemicals and animal feed.<sup>46</sup> The following Table 1.1 shows the production volume<sup>46</sup> and prices<sup>47</sup> of some of the major commodity oils.

Table 1.1 Global production volume and annual average prices for some commodity plant oils for year 2010/11

Plant oil	Production volume (million metric tons)	Prices(US\$/tonne)
Palm	47.83	1154
Soybean	41.23	1306
Rapeseed	23.32	1367
Sunflower	12.20	1404
Palm kernel	5.66	1360
Peanut	5.14	2270
Olive	3.01	2874

Referring to Table 1.1, the three most suitable candidates for industrial application through chemical modification are palm, soybean and rapeseed oil because they are comparatively cheaper than other plant oils and they are available in larger quantity.

### 1.6.1 PLANT OIL CHEMISTRY

Plant oils are part of a larger chemical group known as lipids. Plant oils are also known as triglycerides because they are triesters of glycerol with three fatty acids (Figure 1.29) where the three fatty acids R, R', R'' could be the same fatty acid or could be different. Therefore, the number of triglycerides that could be constructed is enormous due to the many possible combination and permutations of fatty acids that can be reacted with the three hydroxyl groups of glycerol.

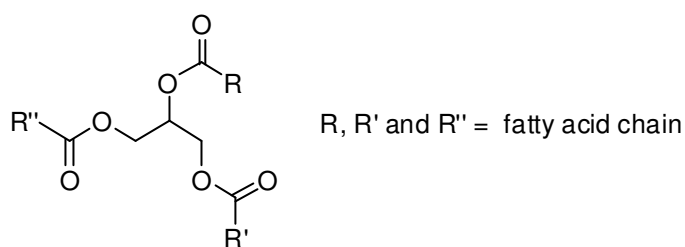


Figure 1.29 General structure of plant oil triglycerides

Generally, the common naturally occurring fatty acids have a hydrocarbon chain length of 12 carbons ( $C_{12}$ ) or more with the most common being derived from  $C_{16}$  and  $C_{18}$  units. The hydrocarbon chain of the fatty acid could be saturated or unsaturated. The common saturated fatty acids<sup>48</sup> are myristic ( $C_{14}$ ), palmitic ( $C_{16}$ ) and stearic ( $C_{18}$ ) acids (Figure 1.30).

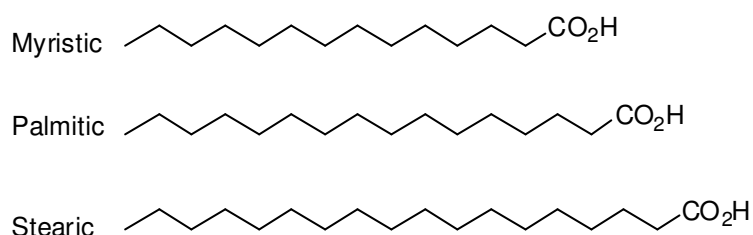


Figure 1.30 Saturated fatty acid

Meanwhile, the most common unsaturated fatty acids<sup>48</sup> are oleic ( $C_{18:1}$ ), linoleic ( $C_{18:2}$ ) and linolenic ( $C_{18:3}$ ) (Figure 1.31), where they respectively have mono-, di-, or tri-unsaturation on the 18 carbon chain. The carbon-carbon double bonds (unsaturation) are usually situated at carbon numbers 9, 12 and 15 and have a *cis* configuration.<sup>48</sup>

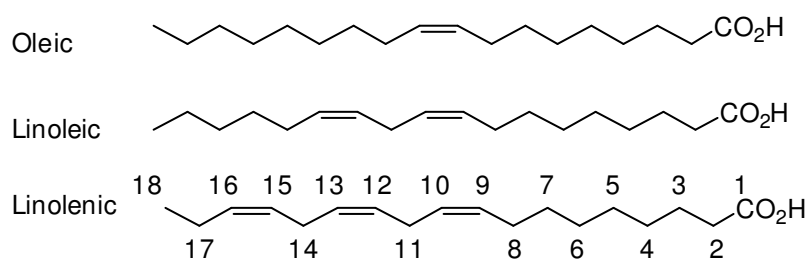


Figure 1.31 Unsaturated fatty acid

The following Table 1.2 shows the fatty acid composition<sup>10</sup> of some of the commodity plant oils.

Table 1.2 Fatty acid composition of major commodity oils

Fatty acid	#C <sup>a</sup> : #DB <sup>b</sup>	Palm (%)	Soybean (%)	Rapeseed (%)	Sunflower (%)	Olive (%)
Lauric	12 : 0	0.2	0.0	0.0	0.0	0.0
Myristic	14 : 0	1.0	0.1	0.2	0.1	0.0
Palmitic	16 : 0	44.4	11.0	4.1	7.0	13.7
Palmitoleic	16 : 1	0.2	0.1	0.3	0.1	1.2
Stearic	18 : 0	4.1	4.0	1.8	4.5	2.5
Oleic	18 : 1	39.3	23.4	60.9	18.7	71.1
Linoleic	18 : 2	10.0	53.2	21.0	67.5	10.0
Linolenic	18 : 3	0.4	7.8	8.8	0.8	0.6
Arachidic	20 : 0	0.3	0.3	0.7	0.4	0.9
Gadoleic	20 : 1	0.0	0.0	1.0	0.1	0.0
Behenic	22 : 0	0.1	0.1	0.3	0.7	0.0
Erucic	22 : 1	0.0	0.0	0.7	0.0	0.0
Lignoceric	24 : 0	0.0	0.0	0.2	0.0	0.0
Avg. #DB/mol oil		1.9	4.6	3.9	4.8	3.8

<sup>a</sup>Number of carbon atoms in fatty acid chain

<sup>b</sup>Number of carbon-carbon double bonds per mol oil

In addition, there are also some rarer fatty acids that are found in nature that bear the epoxy (vernolic) or hydroxyl (ricinoleic) functionalities, (Figure 1.32), which offer different chemical properties to the standard unsaturated fatty acids. However they are not produced in big enough quantities compared to the commodity plant oils to find a place in bulk industrial processes.

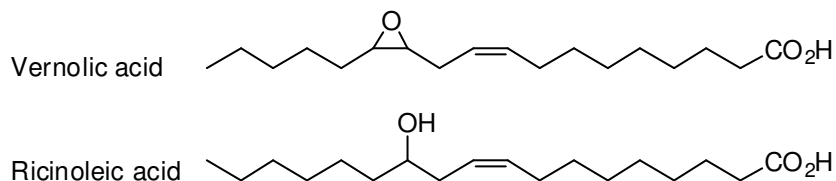


Figure 1.32 Fatty acids with hydroxyl and epoxy functionality

The chemistry of plant oils can be divided into three categories, namely (a) reaction on the hydrocarbon chain, (b) reaction involving the carbonyl group and (c) reaction involving the carbon-carbon double bond. Each of these categories will be discussed in the following section.

### 1.6.2 REACTIONS ON THE FATTY ACID HYDROCARBON CHAIN

For the purpose of the following discussion oleic acid (Figure 1.33) will be used as the model fatty acid.

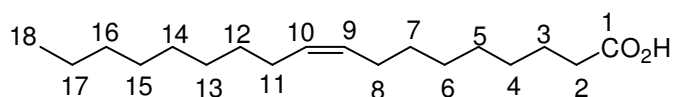


Figure 1.33 Oleic acid

The methylene group next to the carbonyl group (C-2) is activated by the carboxylic acid or the ester functionalities because the carbonyl group can stabilize either a radical or anion generated as an intermediate.<sup>48</sup> Therefore, this  $\alpha$ -methylene group can undergo alpha substitution reaction such as  $\alpha$ -halogenation (Hell-Volhard-Zelensky)<sup>49</sup>,  $\alpha$ -sulfonation<sup>50</sup>, acylation<sup>51</sup>, alkylation<sup>52</sup> and Claisen condensation.<sup>53</sup> The C-8 and C-11 allylic carbons of oleic acid, can be functionalized through allylic hydroperoxidation<sup>54</sup>, allylic hydroxylation<sup>55</sup> and allylic halogenation.<sup>56</sup>

The methyl group (C-18) of oleic acid can be converted to a carboxylic acid directly by both enzymatic and chemical methods. One example of an enzymatic method<sup>57</sup> is the synthesis of 1,18-*cis*-9-octadecenedioic from oleic acid by whole-cell bio-transformation using *C. tropicalis* ATCC20962. Chemical oxidation of the terminal methyl group of methyl oleate with carbon monoxide as the carboxylation source has been achieved to give 1,19-nonadecanedioate. The reaction was conducted at 90 °C under 20 bar pressure of carbon monoxide for 22 hours and catalyzed by a palladium based complex [(dtpbx)Pd(OTf)][OTf].<sup>58</sup>

Substitution at C-3 to C-7 and C-12 to C-16 of oleic acid could theoretically occur with by standard alkane functionalization chemistry (e.g. chlorination). For example, chlorination<sup>59</sup> of myristic acid (Figure 1.34) dissolved in CCl<sub>4</sub> was conducted with gaseous chlorine at 20 °C. A mixture of chlorinated products was obtained with the following distribution according to carbon number: 19.4% (C-3 to C-6), 9% (C-7 to C-11), 9.8% (C-12), 13.8% (C-13) and 3% (C-14). However, this functionalization is not synthetically useful as it is relatively unselective.

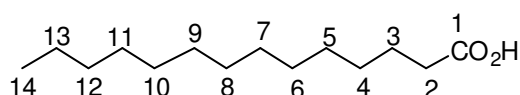


Figure 1.34 Myristic acid

### 1.6.3 REACTIONS INVOLVING THE CARBONYL GROUP

#### Hydrolysis

The hydrolysis of plant oil is the basic chemical reaction of oleochemical industry. Plant oils can be hydrolyzed by water in a process known as fat-splitting that yield free fatty acids and glycerol. This fat-splitting process is usually carried out in continuous mode at 250 °C, under 20-60 bar and uncatalyzed<sup>48</sup> (Figure 1.35).

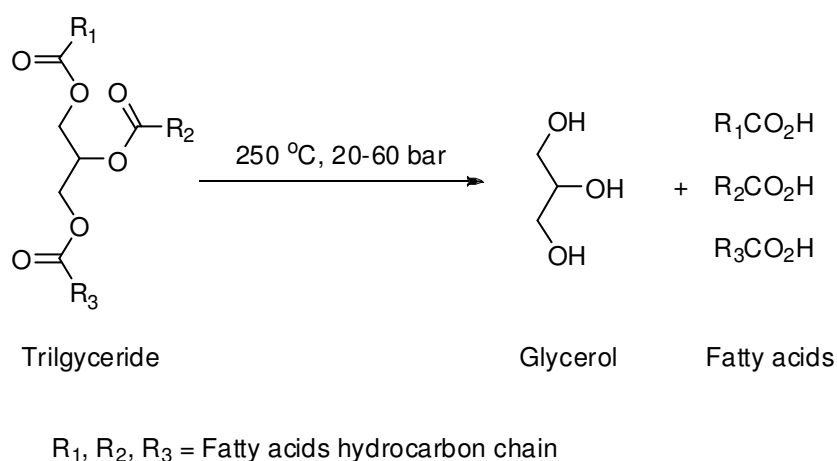


Figure 1.35 Hydrolysis of plant oil

#### Transesterification

The methanolysis of plant oil triglycerides is the process used to produce fatty acid methyl esters, which is bio-diesel. This reaction is usually catalyzed by a basic catalyst such as sodium methoxide or sodium hydroxide. The reaction is generally

(Figure 1.36).

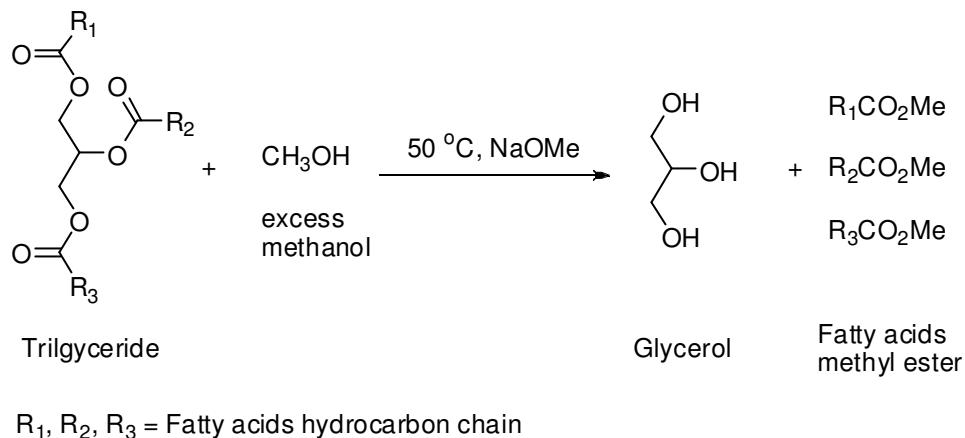


Figure 1.36 Transesterification of plant oil with methanol

## High Pressure Hydrogenation

The high pressure hydrogenation of fatty acid esters is the major commercial production method for the synthesis of alcohol surfactants, typical chain lengths being in the range of C<sub>12</sub> to C<sub>16</sub>. The hydrogenation is typically carried out between 250-275 °C under H<sub>2</sub> pressure of 12-25 MPa with 5% w/w of a metal catalyst. Generally, there are two types of catalysts employed in the high pressure hydrogenation. A CuO/Cr<sub>2</sub>O<sub>3</sub> (1:1) catalyst is employed to reduce both the carbonyl and alkene groups of unsaturated fatty esters to saturated fatty alcohols, while a CuCO<sub>3</sub>/ZnCO<sub>3</sub> (1:1) catalyst is employed to reduce the ester of saturated fatty acids<sup>48</sup> (Figure 1.37).



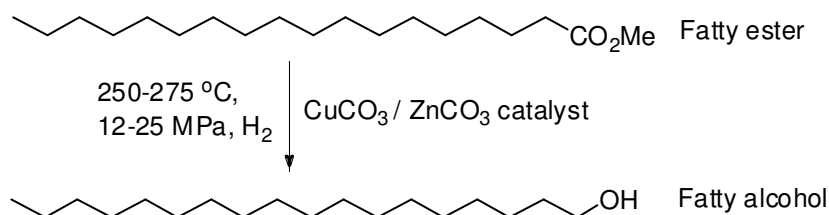
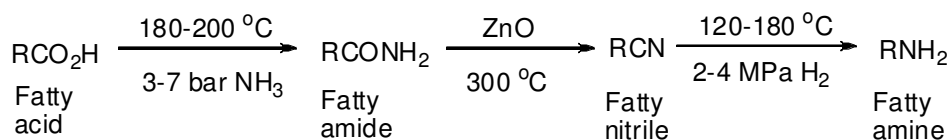


Figure 1.37 High pressure hydrogenation of fatty ester

#### Conversion of fatty acid to fatty amine

The conversion of fatty acid to fatty amine is a three steps reaction. In the first step, the fatty acid is reacted with ammonia at 180-200 °C under ammonia pressure of 3-7 bar to yield fatty amide. In the second step, the fatty amide is dehydrated to fatty nitrile at 300 °C in the presence of zinc oxide as catalyst. The third step involves the hydrogenation of the fatty nitrile catalyze by a Raney- type Ni/Co catalyst at 120-180 °C, 2-4 MPa H<sub>2</sub> to yield fatty amine<sup>60</sup> (Figure 1.38).



R = fatty acid hydrocarbon chain

Figure 1.38 Conversion of fatty acid to fatty amine

### **1.6.4 REACTION ON THE ALKENE GROUP**

Reaction on the alkene group is the second most important type of reaction in the oleochemical industry after the reaction on the carbonyl group.<sup>61</sup> On an industrial scale, the two most important reactions are hydrogenation<sup>62</sup> and epoxidation.<sup>80</sup> Other types of reactions that have been used to produce useful chemicals from unsaturated

plant oils are Friedel-Crafts acylation,<sup>63</sup> oxidative cleavage,<sup>68</sup> hydroxylation,<sup>77</sup> metathesis,<sup>70</sup> thiol-ene<sup>73</sup> and hydroformylation.<sup>76</sup>

In this section, only hydrogenation, and Friedel-Crafts acylation will be discussed while the other mentioned reactions (epoxidation, ozonolysis, hydroxylation, metathesis, thiol-ene and hydroformylation) will be discussed in the following section (plant oil based polyols), in which these reactions are the key process used in the making of the renewable polyols from plant oil.

### Hydrogenation

Hydrogenation is the reaction used to reduce the polyunsaturated fatty acid content of the plant oils and to maintain or increase the content of monounsaturated fatty acid. This reaction is mostly used in the food industry to prepare solid fat (margarine) **(1.11)** from polyunsaturated plant oil such as **(1.10)**. The hydrogenation reaction is conducted at 120 °C under 300 bar of H<sub>2</sub> in the presence of Raney-type nickel catalyst<sup>62</sup> (Figure 1.39).

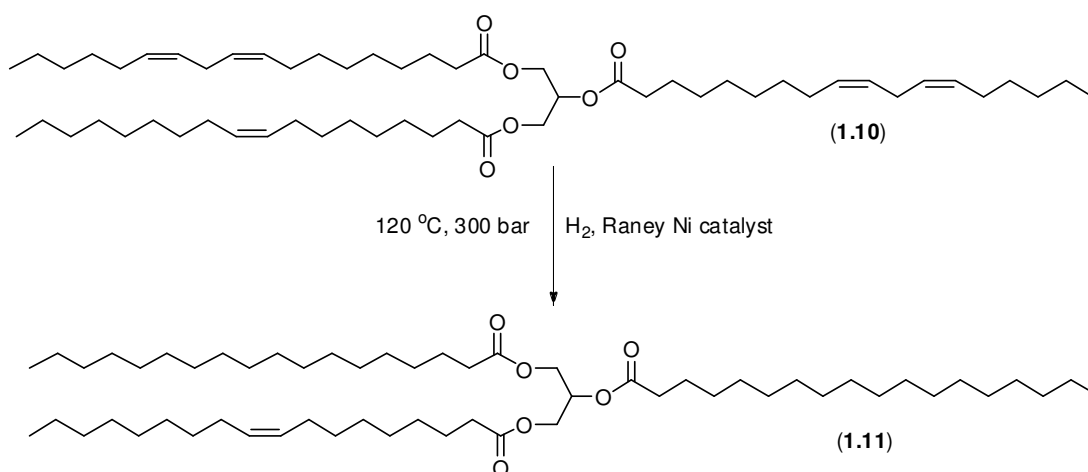


Figure 1.39 Partial hydrogenation of soybean oil

### Friedel-Crafts acylation

The unsaturation of the fatty acid can be functionalized by an electrophilic addition reaction such as a Friedel-Crafts acylation induced by alkylaluminium chlorides. For example, **(1.1)** was acylated with **(1.12)** at room temperature for 2 hours with 2 equivalents of  $\text{EtAlCl}_2$  to yield two isomers<sup>63</sup> **(1.13)** and **(1.14)** in 55% yield (Figure 1.40).

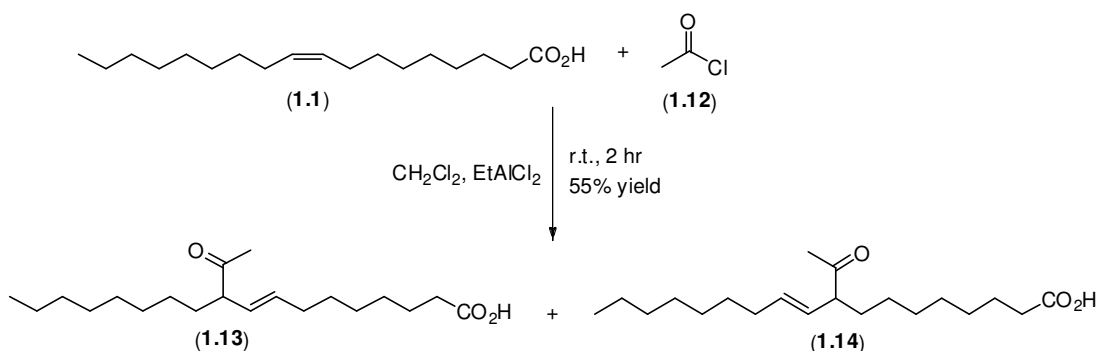


Figure 1.40 Friedel-Crafts acylation of **(1.1)** with **(1.12)**.

The same Friedel-Crafts acylation can be carried out with **(1.15)** to give **(1.16)** and **(1.17)**<sup>63</sup> in isolated yield of 40% (Figure 1.41).

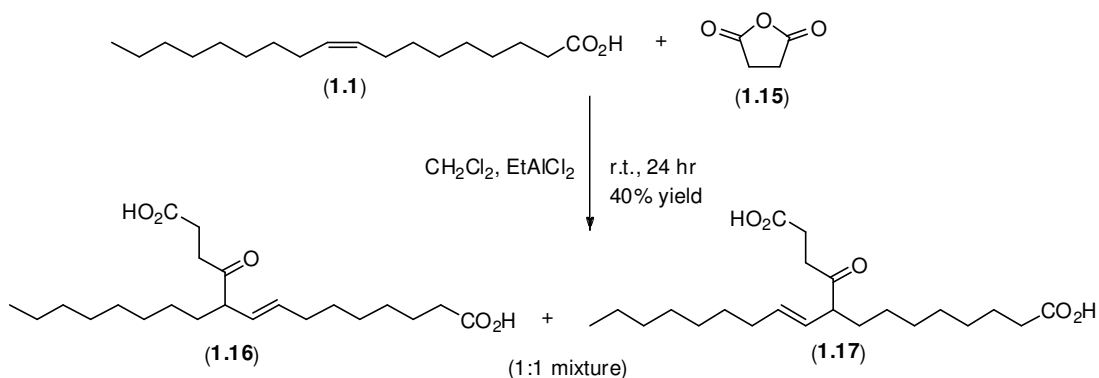


Figure 1.41 Friedel-Crafts acylation of **(1.1)** with **(1.15)**.

## 1.7 PLANT OIL BASED POLYOL

Castor oil is a naturally occurring plant oil that has hydroxyl functionality in its triglyceride molecules (Figure 1.42) and it is mainly used in the production of rigid PU. However, the use of castor oil in PU industry has been limited by its relatively small supply, high cost and the related toxicity of harvesting the castor bean.<sup>64</sup>

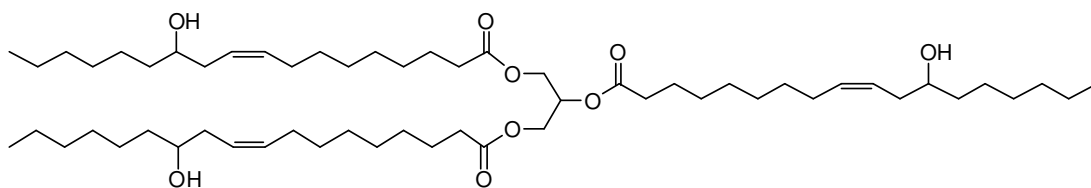


Figure 1.42 Castor oil triglycerides structure

Therefore, scientists have been looking at using other more available and cheaper commodity plant oils such as palm, rapeseed and soybean oil in making polyols. These commodities plant oils were modified chemically to introduce hydroxyl functionality. The chemical modification of plant oils to introduce hydroxyl functionality could be categorized into (a) reaction on the carboxylic group and (b) reaction on the carbon-carbon double bond.

### 1.7.1 PLANT OIL BASED POLYOL FROM REACTION ON THE CARBONYL GROUP

#### Glycerolysis of triglycerides

Glycerolysis is basically the reaction between a plant oil's triglycerides with excess glycerol to yield monoglycerides and diglycerides (Figure 1.43). The monoglycerides and diglycerides have one and two hydroxyl groups per molecule respectively, which can be reacted with diisocyanate to make PU. Glycerolysis can be carried out through chemical<sup>66</sup> or enzymatic<sup>65</sup> pathways.

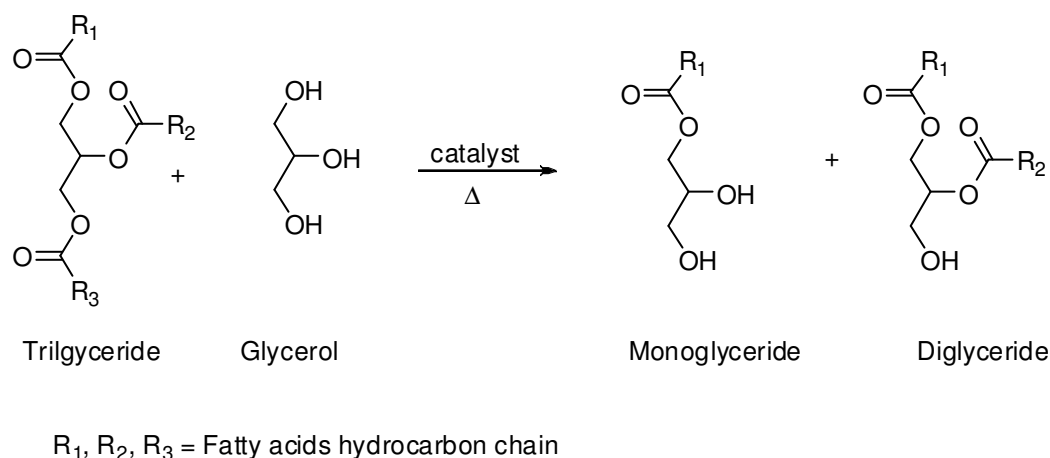


Figure 1.43 Glycerolysis of triglycerides

One example of the enzymatic pathway is the use of Lipozyme IM20 as the glycerolysis catalyst.<sup>65</sup> The enzymatic glycerolysis of triolein was conducted at 40 °C for 3 days to yield 67% monoglycerides and 25% diglycerides.

An example of glycerolysis through the chemical pathway is the reaction between glycerol and soybean oil at 230 °C for 30 minutes with 0.18% NaOH as the catalyst.

The molar ratio between glycerol and soybean oil is 2.5 : 1 and this reaction yielded 58% monoglyceride and 33% diglycerides.<sup>66</sup>

### Transamidation

Transamidation is another method to make plant oil based polyols through reaction between triglycerides and amine compounds. For example, **(1.18)** was reacted with **(1.19)** in the presence of sodium methoxide as the catalyst at 110 °C catalysed for 6 hours to yield **(1.20)** and **(1.21)**<sup>67</sup> (Figure 1.44).

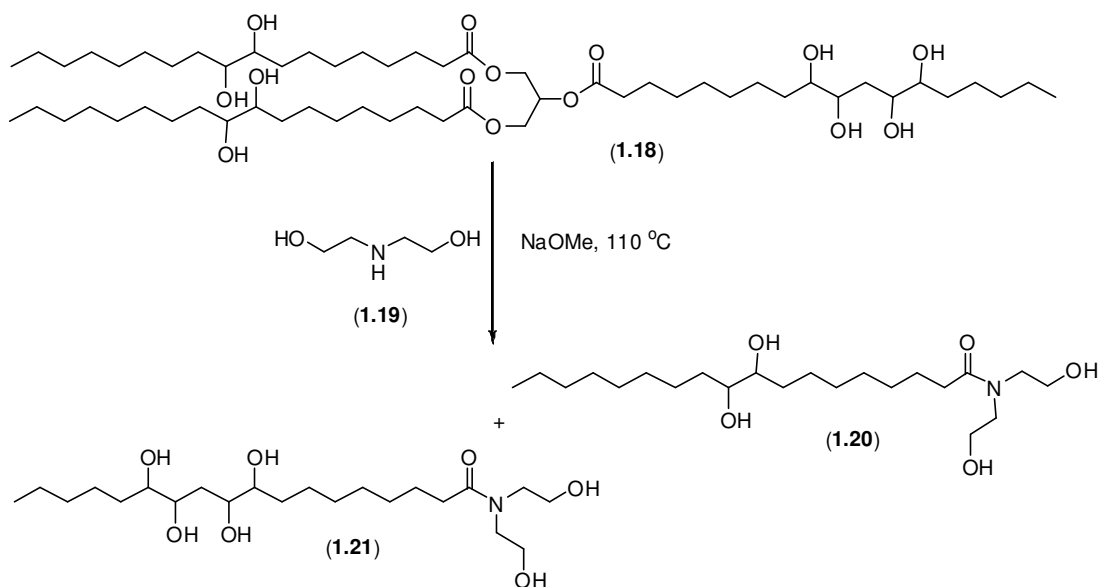


Figure 1.44 Transamidation of **(1.18)** with **(1.19)**

## **1.7.2 PLANT OIL BASED POLYOL FROM REACTIONS ON THE ALKENE GROUP**

There are several key reactions involving the alkene group (unsaturation) that are used on industrial and laboratory scale to make plant oil based polyol. These key

reactions are ozonolysis,<sup>48</sup> direct hydroxylation,<sup>77</sup> metathesis,<sup>70</sup> thiol-ene,<sup>73</sup> hydroformylation<sup>76</sup> and epoxide ring-opening.<sup>86</sup> Each of these reactions will be discussed in the following section.

### Ozonolysis

Oxidative cleavage of the unsaturation of fatty acids or triglycerides by ozone is a clean method to produce difunctional or trifunctional compounds because it does not require a catalyst and there is no spent oxidant to be handled after completion of the reaction. However, due to the hazard of ozone, the only industrial application of ozonolysis in the fats and oils industry is in the production of **(1.22)** and **(1.23)** from **(1.1)**<sup>48</sup> (Figure 1.45). The **(1.22)** can be reduced to **(1.24)** by a standard hydrogenation<sup>68</sup> process and this diol can be used to make PU (Figure 1.46).

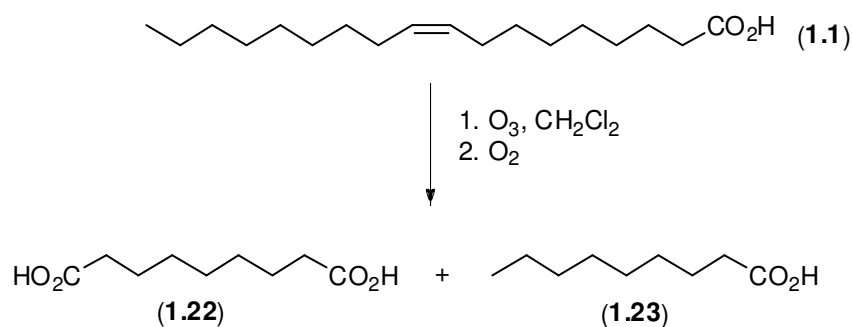


Figure 1.45 Ozonolysis of **(1.1)**

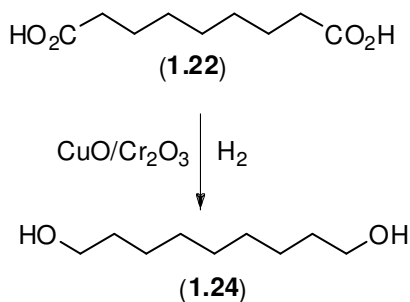


Figure 1.46 Hydrogenation of **(1.22)**

The same ozonolysis can be applied to unsaturated triglyceride molecules and after reduction of the products from the ozonolysis reaction; the resultant compounds will have hydroxyl functionality. For example, **(1.10)** was subjected to ozonolysis at -40 °C with subsequent reduction of the ozonolysis products with NaBH<sub>4</sub> at 10 °C to yield **(1.25)**, **(1.26)** and **(1.27)**<sup>69</sup> (Figure 1.47).

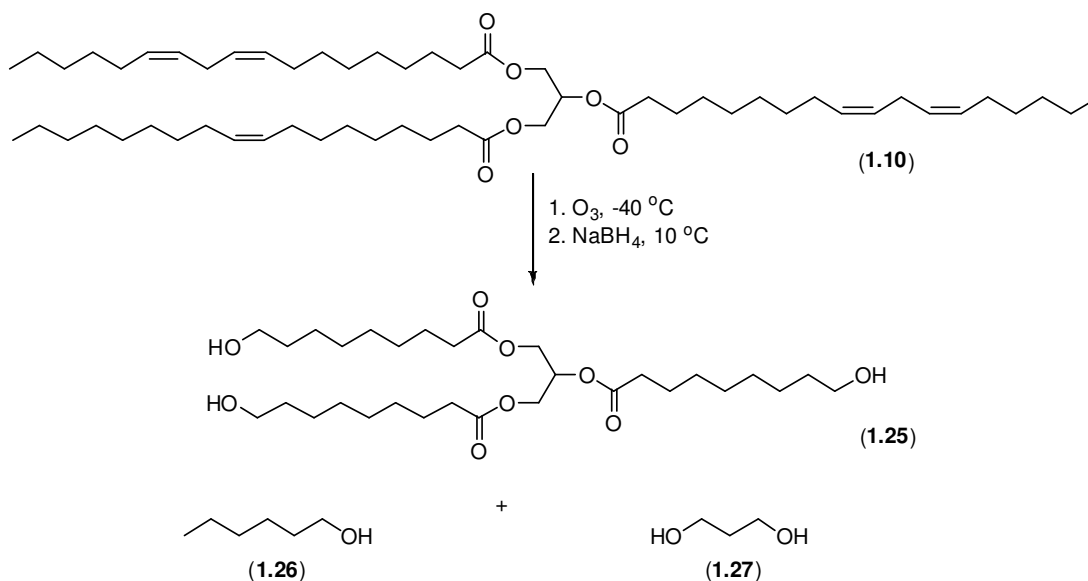


Figure 1.47 Ozonolysis of **(1.10)** and subsequent reduction of ozonolysis products

### Metathesis

The unsaturated fatty acid can be subjected to self-metathesis reaction to give  $\alpha,\omega$ -diacid. For example, **(1.1)** was self-metathesized at 40 °C for 24 hours in the presence of second generation Grubbs catalyst to yield **(1.28a)** in 64% yield and a long chain alkene **(1.28b)** as a co-product (Figure 1.48).

In subsequent reaction, **(1.28a)** was reduced to diol **(1.29)** by reaction with LiAlH<sub>4</sub> at room temperature<sup>70</sup> (Figure 1.48). The diol was used to make thermoplastic PU that exhibited a melting point at 130 °C.



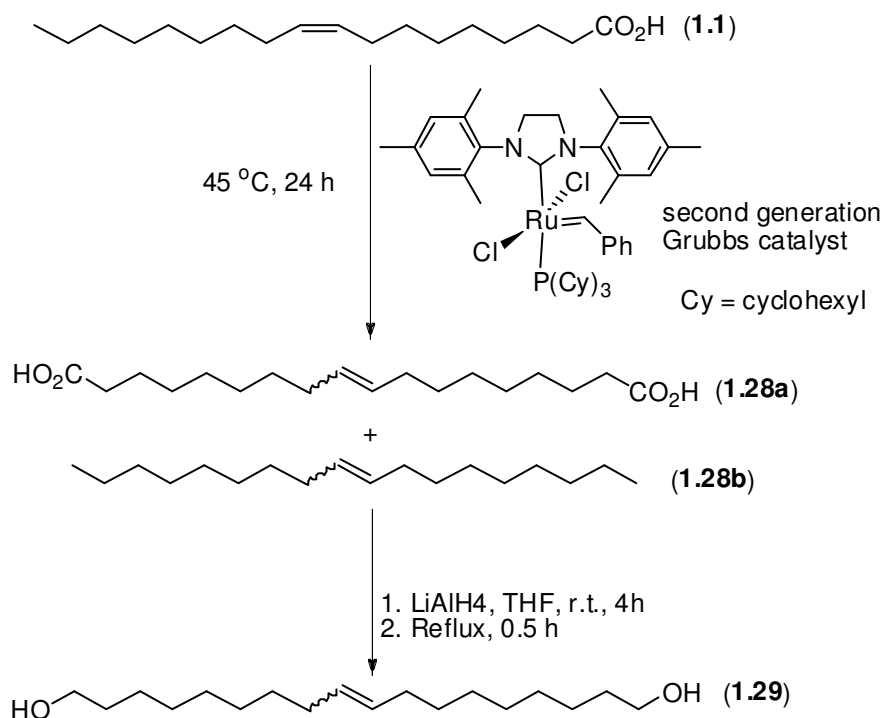


Figure 1.48 Self-metathesis of **(1.1)** and subsequent reduction to **(1.29)**

### Thiol-ene

The thiol-ene reaction was introduced by Sharpless and coworkers<sup>71</sup> as click chemistry, which is a versatile reaction used in polymer synthesis.<sup>72</sup> The thiol-ene reaction has been used to convert the unsaturation of plant oils into hydroxyl groups in order to make polyols from plant oils.

For example, **(1.30)** was reacted with an excess of **(1.31)** in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photo-initiator. The mixture was irradiated with an ultraviolet lamp ( $\lambda = 365 \text{ nm}$ ) for few minutes to yield a number of isomers of hydroxylated compounds **(1.32)** and **(1.33)** as a mixture.

Subsequently, the ester functionality of the hydroxylated compounds was reduced with  $\text{LiAlH}_4$  to yield dihydroxylated compounds (**1.34**) and (**1.35**) as a mixture of isomers) that were used as monomers for PU synthesis<sup>73</sup> (Figure 1.49).

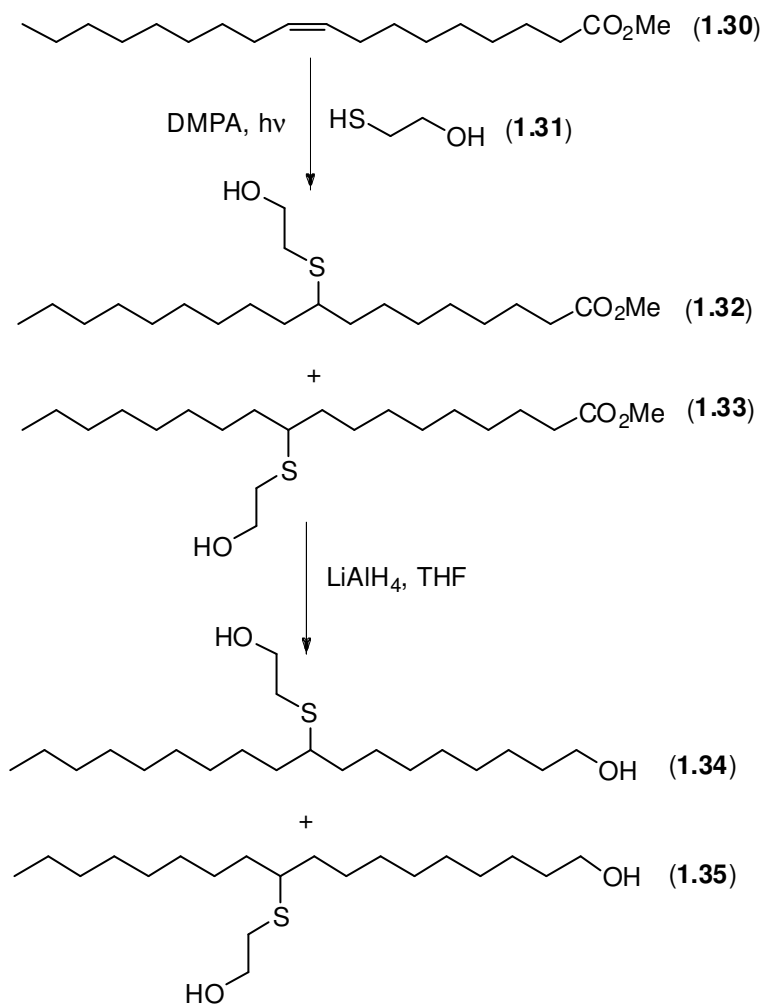


Figure 1.49 Dihydroxylated compound (**1.34**) and (**1.35**) from (**1.30**) through thiol-ene and reduction reactions

The thiol-ene reaction can also be applied to unsaturated plant oil triglycerides. An example of this is the reaction between (**1.36**) and (**1.31**) at 20 °C for 1 hour under UV irradiation ( $\lambda = 250\text{-}450\text{ nm}$ ) to yield (**1.37**) (Figure 1.50) that can be used as polyol<sup>74</sup> for PU synthesis.

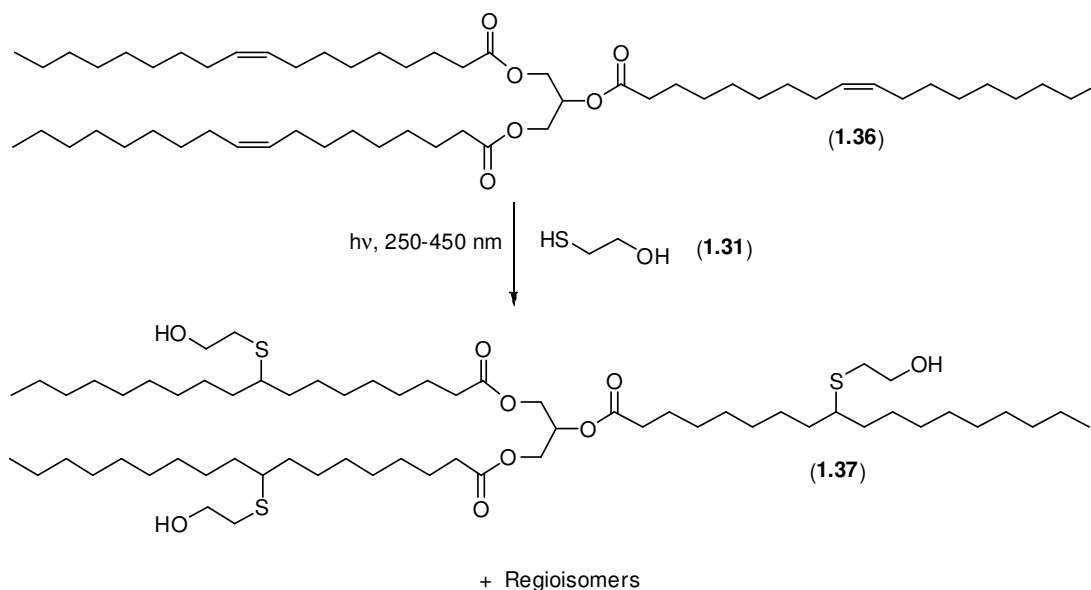


Figure 1.50 Synthesis of **(1.37)** through thiol-ene reaction

### Hydroformylation

Dow Chemical has patented a process to make polyol from plant oil derivatives.<sup>75</sup> In the first step of the process, **(1.30)** was subjected to a hydroformylation reaction, in which the **(1.30)** was reacted with a 1:1 mixture of carbon monoxide and hydrogen gas in the presence of rhodium based catalyst. The hydroformylation reaction was conducted at 90 °C under 2.8 MPa pressure for 23 hours to yield the desired product **(1.38)**<sup>76</sup> and regioisomer (Figure 1.51).

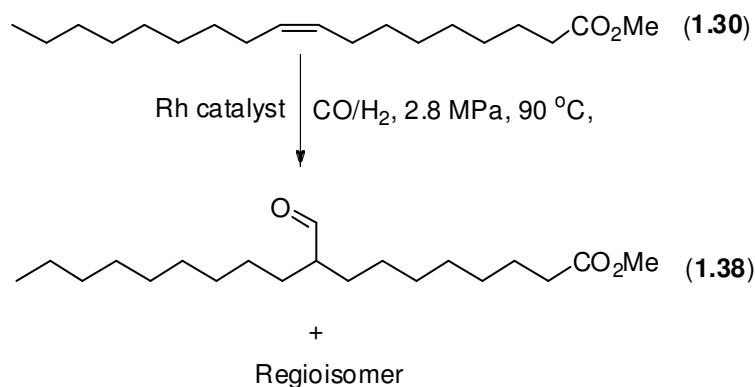


Figure 1.51 Hydroformylation of **(1.30)** to **(1.38)**

The **(1.38)** was subjected to a reduction reaction with hydrogen gas in the presence of a nickel based catalyst at 140 °C under 5.7 MPa of hydrogen gas pressure. As a result of this reduction reaction, the **(1.38)** was reduced to **(1.39)**, thus creating a hydroxylated fatty ester **(1.39)**<sup>76</sup> (Figure 1.52).

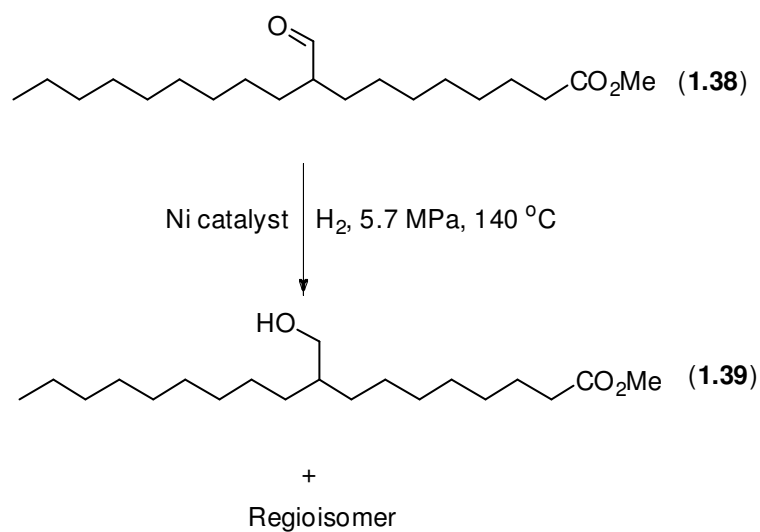


Figure 1.52 Reduction of the **(1.38)** to **(1.39)**

The **(1.39)** was transesterified with a poly(ethylene oxide) triol (average molecular weight of 600) (PEG 600 triol) in the presence of stannous octoate as the catalyst at 200 °C under reduced pressure to remove methanol from reaction system. The

product from this transesterification reaction was **(1.40)**<sup>75</sup> that has an average molecular weight of 3100 (Figure 1.53) and this plant oil based polyol can be used to make PU products.

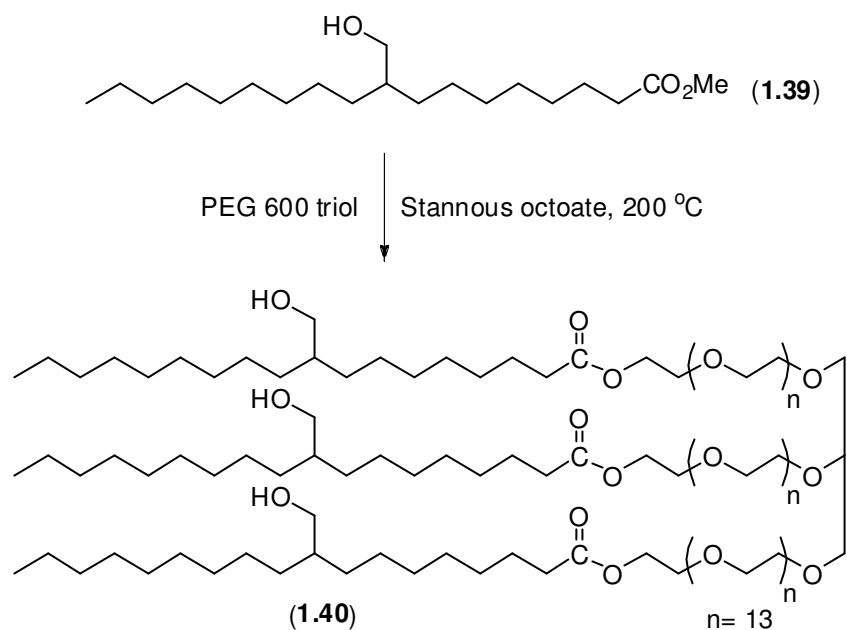


Figure 1.53 Plant oil based polyol **(1.40)** from transesterification of **(1.39)** with PEG 600 triol

#### Direct hydroxylation

Polyols can also be made from unsaturated plant oil triglycerides through direct conversion of the unsaturation to hydroxyl functionality. An example of this is the transition metal catalyzed vicinal hydroxylation of **(1.30)** with H<sub>2</sub>O<sub>2</sub>. One of the methods utilized rhenium (VII) oxide (Re<sub>2</sub>O<sub>7</sub>) as the catalyst for the vicinal hydroxylation of **(1.30)** with 60% H<sub>2</sub>O<sub>2</sub>. The reaction was conducted in 1,4-dioxane at 40 °C for 16 hour to yield 80% **(1.41)**<sup>77</sup> (Figure 1.54).

Direct vicinal hydroxylation of (**1.30**) was also achieved with tungstic acid<sup>78</sup> ( $\text{H}_2\text{WO}_4$ ) as the catalyst and by using 70%  $\text{H}_2\text{O}_2$  as the oxidant. The reaction was conducted at 50 °C for 3 hours and yielded 75% (**1.41**) (Figure 1.54).

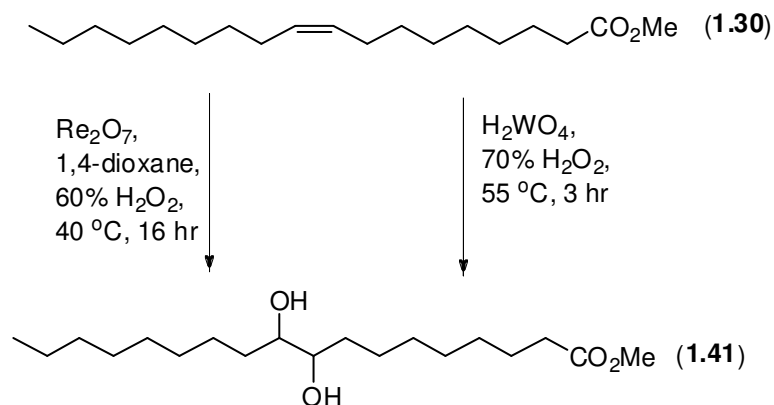


Figure 1.54 Direct vicinal hydroxylation of (**1.30**)

Direct hydroxylation can also be applied to unsaturated plant oil such as (**1.42**). The direct hydroxylation of (**1.42**) was carried out in acidic condition ( $\text{H}_3\text{PO}_4$ ) at 100 °C for 6 hours with 30%  $\text{H}_2\text{O}_2$  as the oxidant. The reaction was catalyzed by tungsten powder and a phase transfer catalyst (Adogen 464). The reaction yielded 70% (**1.43**)<sup>79</sup> (Figure 1.55).

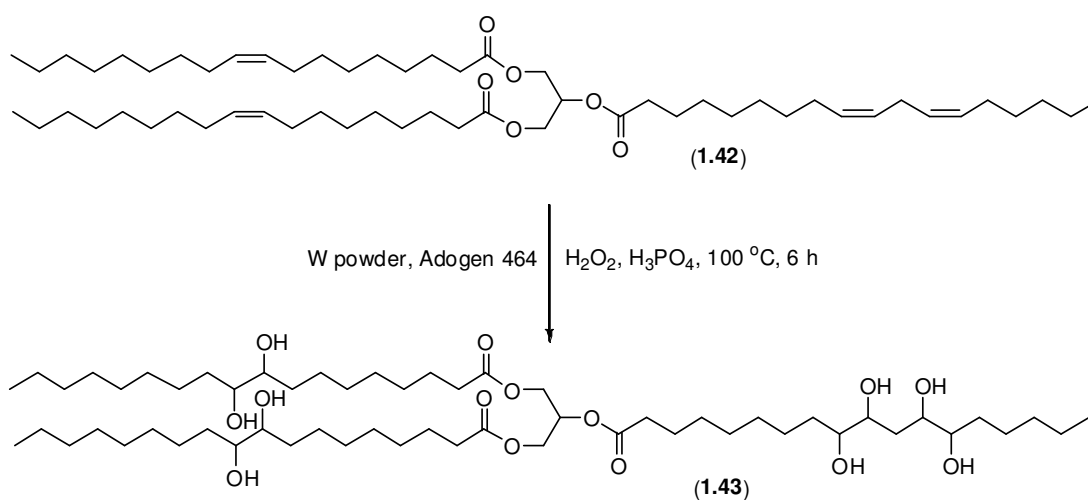


Figure 1.55 Direct hydroxylation of (**1.42**)

### Epoxidation and epoxide ring-opening

On an industrial scale, the epoxidation of unsaturated plant oils such as (**1.44**) is carried out through the Prileshajev reaction to yield (**1.45**), in which a peroxy acid is the epoxidation agent generated from a short-chain organic acid such as formic acid<sup>80</sup> (Figure 1.56).

The performic acid can be generated in a separate step or *in situ* with hydrogen peroxide as the oxidant. However, the formic acid is sufficiently acidic to cause side reactions by ring opening of the formed epoxide group<sup>81</sup>. Therefore, the selectivity of this process seldom exceeds 80%.

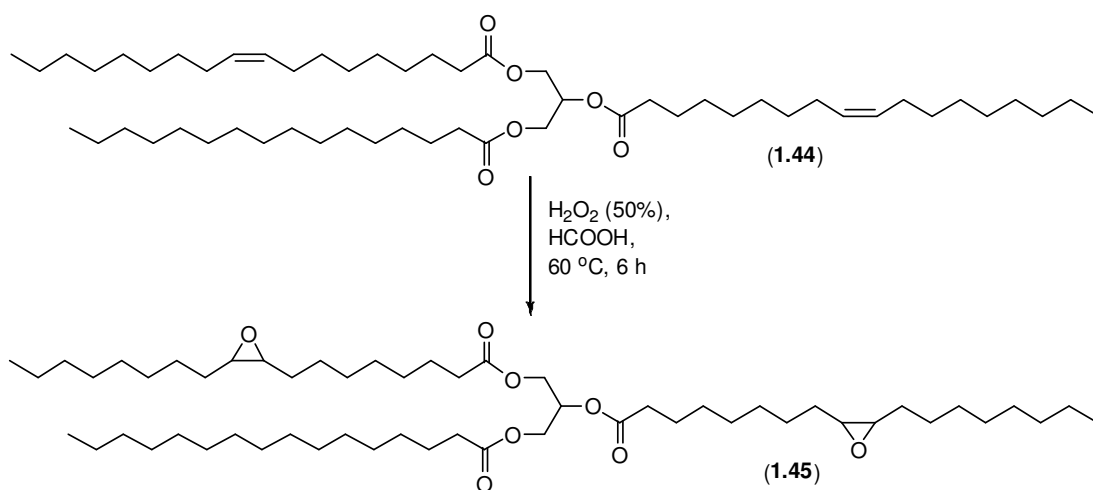


Figure 1.56. Epoxidation of (**1.44**) with formic acid and hydrogen peroxide

The epoxidation of unsaturated fatty acids or esters with hydrogen peroxide as the oxidant can also be conducted with transition metal compounds as the catalyst such as methyltrioxorhenium<sup>82</sup> ( $\text{CH}_3\text{ReO}_3$ ) in an organic solvent system with quaternary ammonium peroxy phosphotungstate<sup>83</sup>  $[\text{((C}_6\text{H}_{13})_4\text{N)}_3^+ \cdot (\text{PO}_4(\text{W}(\text{O})(\text{O}_2)_2)_4)^{3-}]$  in a two phase system.

The epoxidation of (**1.46**) catalyzed by methyltrioxorhenium was conducted in pyridine at room temperature for 4 hours and yielded 88% (**1.47**) (Figure 1.57). Meanwhile, the quaternary ammonium peroxy phosphotungstate catalyzed epoxidation reaction of (**1.1**) was conducted in two phase system (oleic acid-H<sub>2</sub>O<sub>2</sub>) at 60 °C for 1 hour to yield 89% (**1.48**) (Figure 1.58).

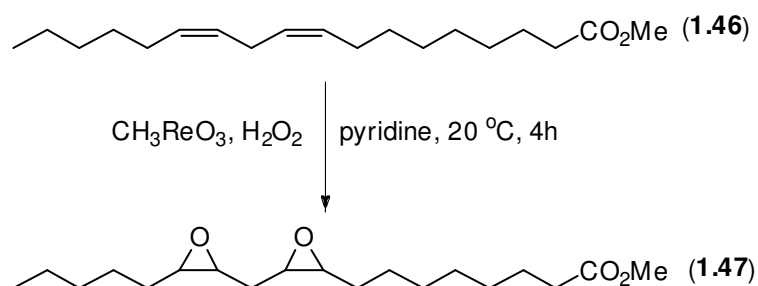


Figure 1.57 Epoxidation of (**1.46**) catalyzed by methyltrioxorhenium

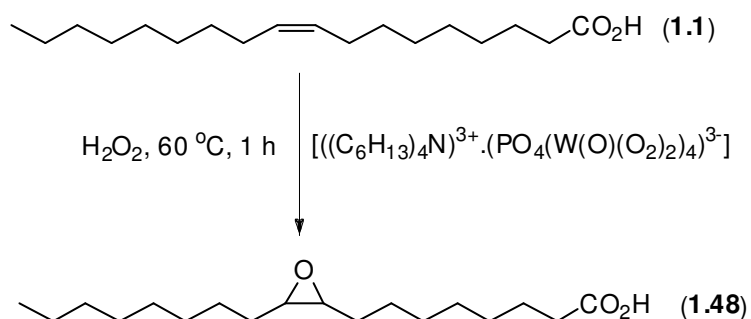


Figure 1.58 Epoxidation of (**1.1**) catalyzed by quaternary ammonium peroxy phosphotungstate

The epoxidized plant oils and fatty acids or esters can be subjected to epoxide ring-opening reactions to give polyols that can be used in PU synthesis. The epoxide ring can be cleaved by a wide range of nucleophilic reagents such as water, alcohols, amines and thiols.<sup>84</sup>



Guo *et al.* reported the epoxide ring-opening of **(1.49)** with water<sup>85</sup> to produce polyols. The reaction was conducted in a mixture of solvent and water (*t*-butanol : water) at 85 °C for 6 hours and the reaction was catalyzed by phosphoric acid. The products from this reaction consist of **(1.50)** and a significant amount of oligomers **(1.51)** (Figure 1.59).

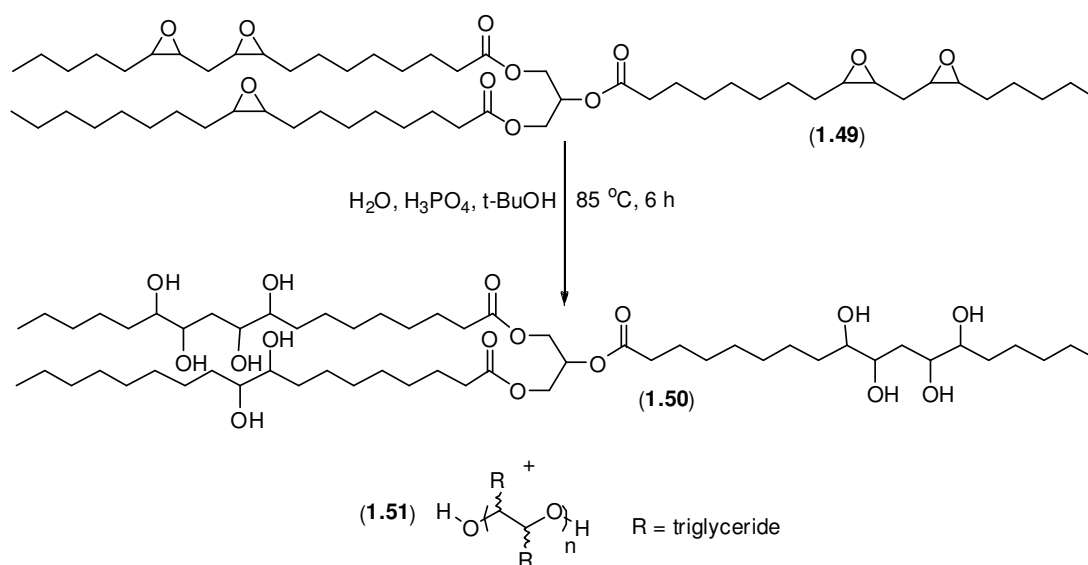


Figure 1.59 Epoxide ring-opening of **(1.49)** with water

Abraham *et al.* disclosed a process to make polyols from **(1.49)** by epoxide ring-opening in methanol<sup>86</sup> at 65 °C for 1 hour and the reaction was catalyzed by fluoroboric acid ( $\text{HBF}_4$ , 48% in water). The reaction yielded 80% **(1.52)** and 20% **(1.51)** (Figure 1.60).

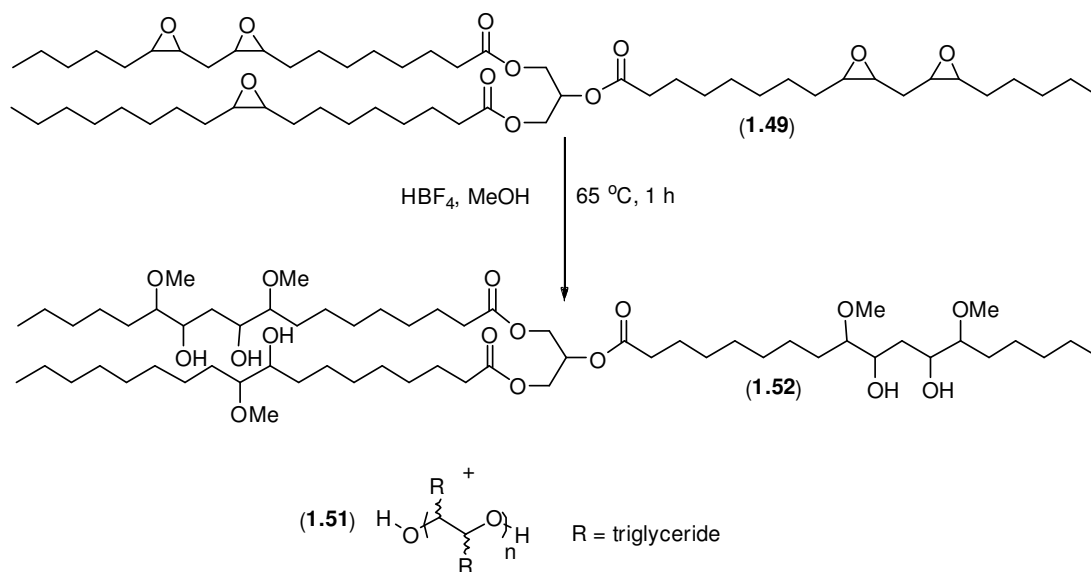


Figure 1.60 Epoxide ring-opening of **(1.49)** with methanol

The epoxide ring of the epoxidized plant oil can also be opened by a carboxylic acid group<sup>87</sup> as disclosed by Miao *et al.* in which **(1.49)** was subjected to ring opening with **(1.53)** without any catalyst at 90 °C for 6 hours. The reaction yielded 70% **(1.54)** (Figure 1.61).

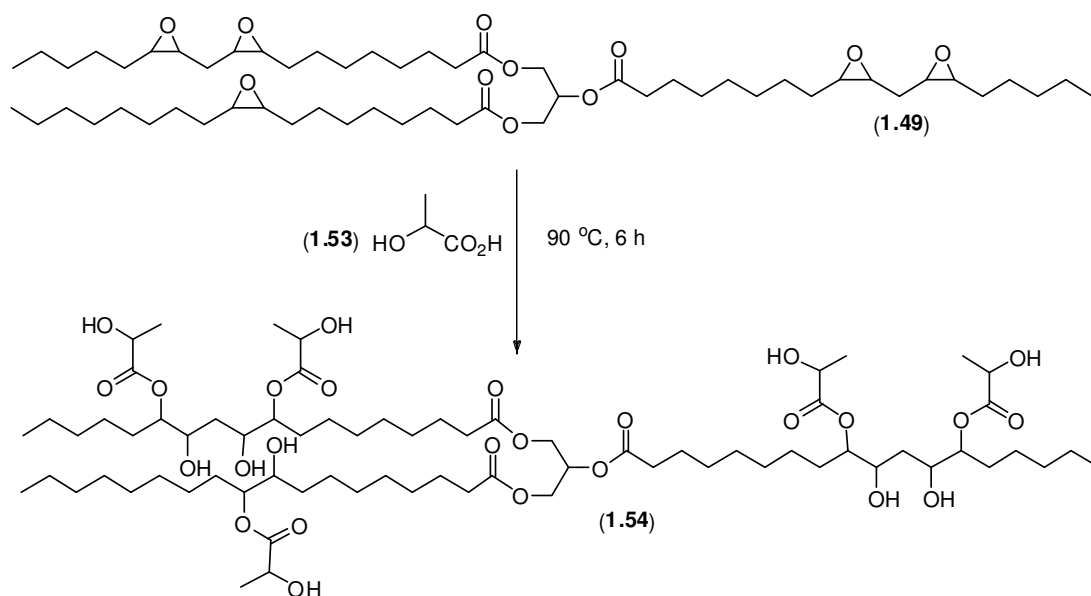


Figure 1.61 Ring opening of **(1.49)** with **(1.53)**

Biswas *et al.* disclosed a method to ring-open the epoxide group of **(1.49)** with **(1.55)**.<sup>88</sup> The reaction was conducted at 90 °C for 4 hours and was catalyzed by ZnCl<sub>2</sub>. The reaction yielded 80% **(1.56)** (Figure 1.62). The reaction parameters (temperature, time) as well as the choice of amine and catalyst were optimized to favor the epoxide ring-opening reaction instead of the competing transamidation reaction.

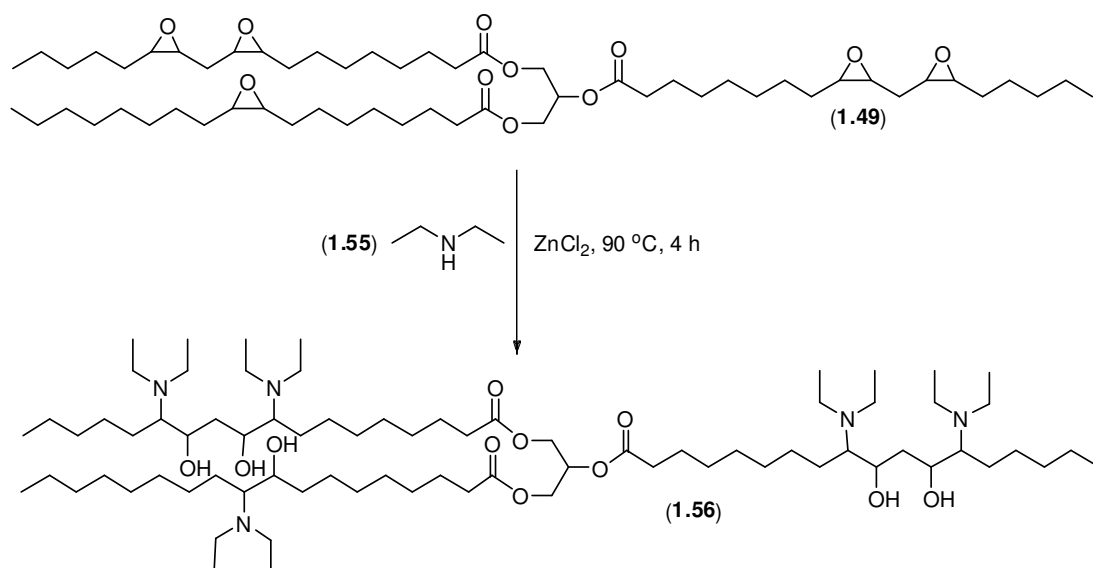


Figure 1.62 Ring opening of **(1.49)** with **(1.55)**

## 1.8 SUMMARY

PU are a versatile class of polymer and PU products can be easily found in our daily life. PU products can be classified into foam products (flexible and rigid), elastomers, coatings, adhesives and sealant. Generally, PUs are made from the reaction between diisocyanate and polyol. Commercially, both the diisocyanate and the polyol are produced from non-renewable petroleum based chemicals. However, due to consumer demand for more environmental friendly products and higher prices of petroleum oil, many reactions have been carried out globally to synthesize polyols and diisocyanates from renewable resources.

In this introduction chapter, I have highlighted various types of renewable resources used in making polyols and diisocyanates. Plant oil is one of the bountiful renewable resources used to synthesize both the diisocyanates and polyols. Plant oils are converted to diisocyanates and polyols through chemical modifications on the unsaturation and ester functionalities of the plant oil. One of the frequently used synthetic methods to make plant oil based polyol is the epoxidation of unsaturation of plant oil and subsequent epoxide ring-opening with nucleophiles. However, most of the reported plant oil based polyols are monomeric macromonomers, which are basically a single unit of polyhydroxylated triglycerides that have molecular weight in the range of 1000-1500 Da such as **(1.50)** (Figure 1.63).

Therefore, in the next few chapters, the synthesis of oligomeric/polymeric polyols from plant oils such as **(1.51)** (Figure 1.63) and the evaluation of properties of PU

products prepared from this oligomeric/polymeric plant oil based polyols will be discussed.

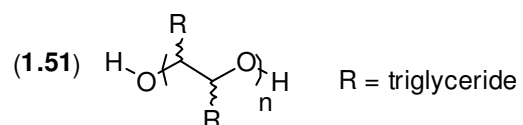
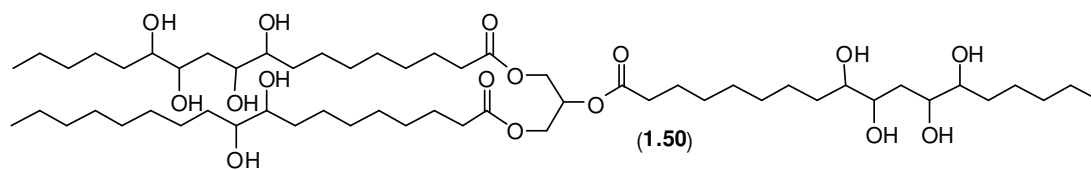


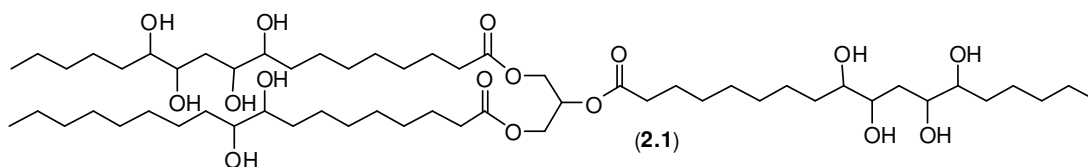
Figure 1.63 Monomeric macromonomers and oligomeric/polymeric polyols

## CHAPTER 2 – OLIGOMERS FROM EPOXIDIZED PLANT OILS

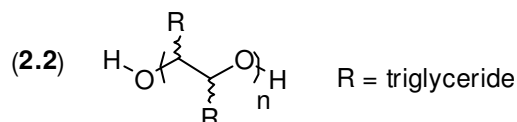
### 2.0 INTRODUCTION

Generally, commercially available petro-chemical based polyols have a molecular weight in the range of 400 to 10000 Dalton (Da). The low molecular weight polyols (400 to 1000 Da) with high functionality (3-8 hydroxyl group per mol) are suitable for making rigid polyurethane, while the high molecular weight polyols (2000 to 10000) with low functionality (2-3 hydroxyl group per mol) are suitable for making flexible/elastomeric polyurethane.<sup>10</sup>

Most of the reported literature on plant oil based polyols focuses on making monomeric plant oil based polyols, which are basically a single unit of a polyhydroxylated triglyceride molecule such as **(2.1)**<sup>89</sup> that have a molecular weight in the range of 1000-1500 Da, which are suitable for making rigid PUs.



Not many literature reports have appeared on making oligomeric/polymeric polyols such as **(2.2)** from plant oil and its derivatives. One of the examples is the work done by Lligadas *et al.*, where the epoxidized methyl oleate **(2.3)**<sup>90</sup> was oligomerized through epoxide ring-opening polymerization at room temperature by using HSbF<sub>6</sub> as the catalyst (Figure 2.1).



Subsequently, the ester functionality of the oligomerized methyl oleate (**2.4**) was reduced to a hydroxyl group with  $\text{LiAlH}_4$  in THF in order to yield oligomeric polyols (**2.5**) with higher hydroxyl functionality (3-4 hydroxyl per mol) that have molecular weight in the range of 1000 to 1500 Da (Figure 2.1), which are suitable for rigid PUs.

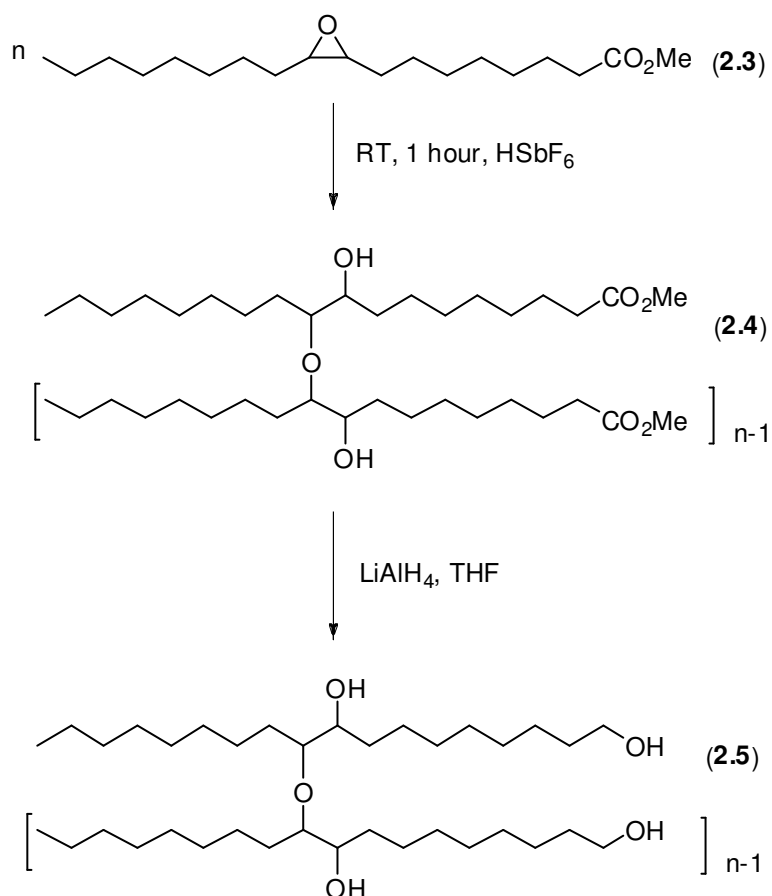


Figure 2.1 Oligomerization of (**2.3**) and subsequent reduction

Epoxide ring-opening polymerization has also been performed on epoxidized plant oil triglycerides. For example, Liu *et al.* reported the epoxide ring-opening polymerization of epoxidized soybean oil (**2.6**) in dichloromethane catalyzed by boron trifluoride diethyl etherate ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) at  $0^\circ\text{C}$  for 3 hours<sup>91</sup> (Figure 2.2).

The products from this reaction were cross-linked polymers (**2.7**), which were insoluble in many common solvents. The cross-linked polymers were hydrolyzed to make hydrogels for pharmaceutical applications. However, the cross-linked polymers are not suitable for making PU due to their cross-linked nature.

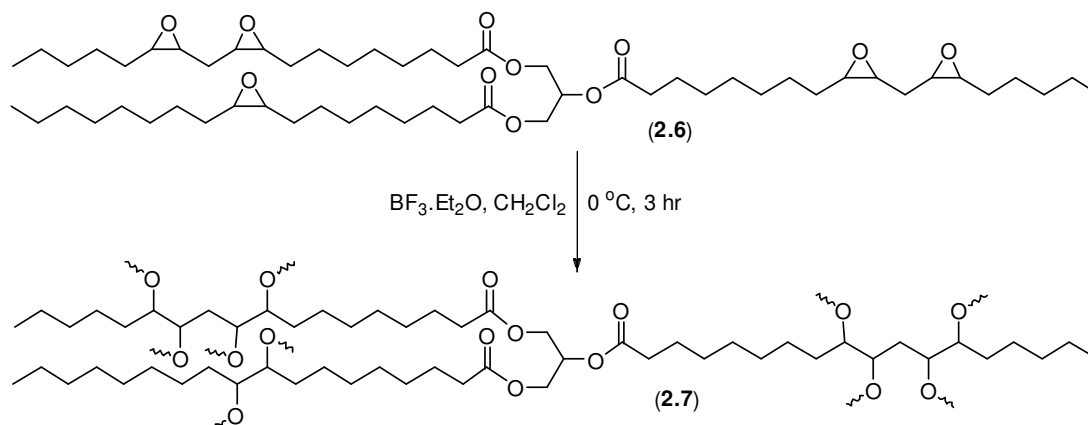


Figure 2.2. Cross-linked polymer (**2.7**) from epoxide ring-opening polymerization of (**2.6**).

*Therefore, one of the aims of this chapter is to produce oligomeric polyols from epoxidized plant oils through epoxide ring-opening polymerization without forming the cross-linked polymers. The successfully oligomerized epoxidized plant oils will give access to plant oil based polyols with high molecular weight and low hydroxyl functionality that are suitable for making flexible polyurethanes.*

In this chapter, I have prepared epoxidized plant oils by using tungsten powder as the catalyst and hydrogen peroxide as the oxidant in the presence of a phase transfer catalyst.<sup>83</sup> The prepared epoxidized plant oils were subjected to ring-opening polymerization to yield polyols that can be used for making PUs. The preparation of epoxidized plant oils and subsequent ring-opening polymerization of the epoxidized plant oils will be discussed in detail in the following sub-sections.



## 2.1 ANALYSIS OF PLANT OILS

The starting materials (plant oils and fatty acid methyl ester) for this project are methyl oleate (**2.8**), cocoa butter (**2.9**), palm oil (**2.10**), rapeseed oil (**2.11**) and soybean oil (**2.12**). These starting materials were analyzed by gas chromatography<sup>92</sup> to determine their fatty acid composition (FAC). The result of the analysis was tabulated in Table 2.1

Table 2.1. Fatty acid composition of the starting materials (see Figure 2.3)

Fatty acid	#C <sup>a</sup> : #AG <sup>b</sup>	( <b>2.8</b> ) (%)	( <b>2.9</b> ) (%)	( <b>2.10</b> ) (%)	( <b>2.11</b> ) (%)	( <b>2.12</b> ) (%)
Lauric	12 : 0	0.0	0.0	0.0	0.0	0.0
Myristic	14 : 0	0.5	0.0	0.0	0.0	0.0
Palmitic	16 : 0	6.5	25.8	42.0	5.4	11.4
Palmitoleic	16 : 1	6.0	0.3	0.0	0.2	0.0
Stearic	18 : 0	2.0	37.9	3.8	2.0	4.0
Oleic	18 : 1	77.0	32.2	43.4	61.2	23.1
Linoleic	18 : 2	7.4	2.9	10.0	19.0	54.2
Linolenic	18 : 3	0.0	0.0	0.4	9.6	7.3
Arachidic	20 : 0	0.0	0.9	0.4	0.6	0.0
Gadoleic	20 : 1	0.6	0.0	0.0	1.4	0.0
Behenic	22 : 0	0.0	0.0	0.0	0.3	0.0
Erucic	22 : 1	0.0	0.0	0.0	0.0	0.0
Lignoceric	24 : 0	0.0	0.0	0.0	0.3	0.0
Avg. #AG <sup>b</sup> /mol oil		1.1	1.1	1.9	4.0	4.7

<sup>a</sup>Number of carbon in fatty acid chain

<sup>b</sup>Number of alkene group per mol oil

The FAC analysis by gas chromatography enables us to calculate the theoretical average alkene group per mol of oil. The information from this analysis also indicates the most abundant structure for the respective starting materials. Further

analysis with electro-spray ionization (ESI) mass spectrometry and  $^1\text{H}$  NMR suggested the following structures (Figure 2.3) as the most abundant triglycerides respectively in the starting materials.

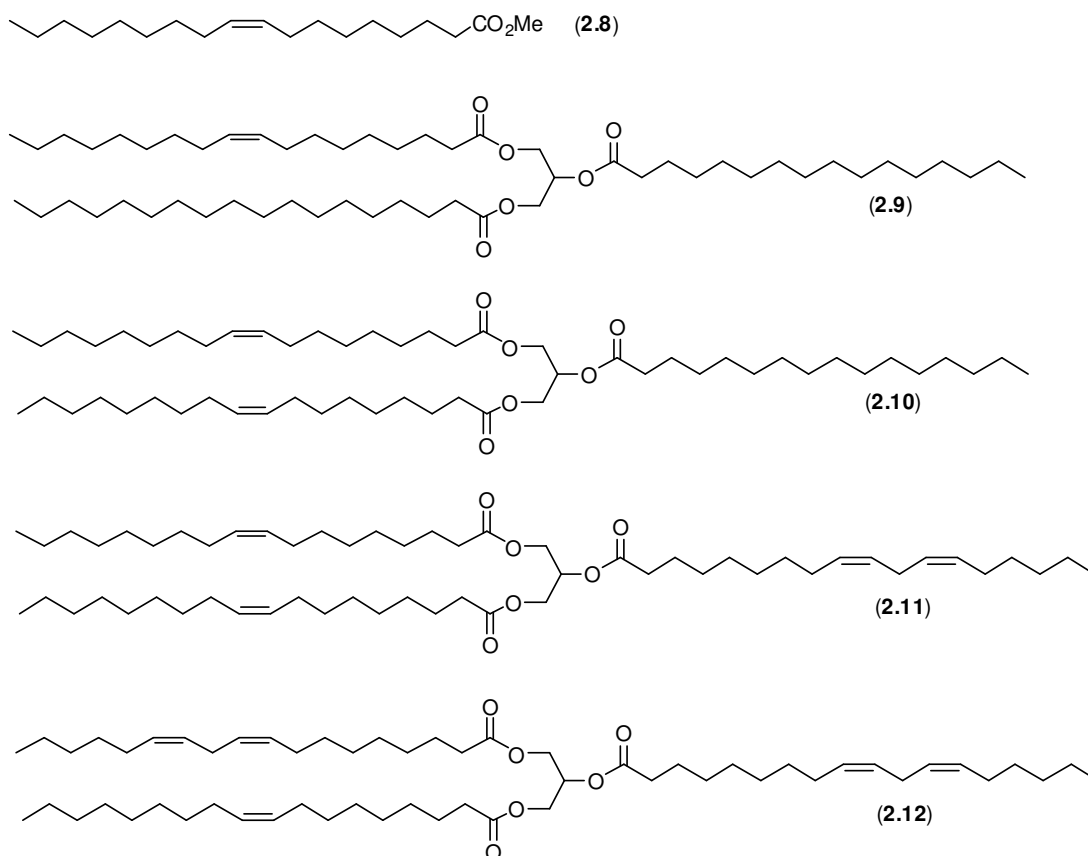


Figure 2.3 Most abundant triglycerides and fatty acid methyl ester structures for respective raw materials

The selected plant oils differ in the degree of unsaturation present and range from one to five alkene groups per molecule. These plant oils were chosen because the different level of unsaturation of the respective plant oils will enable the study on the effect of plant oil structure/unsaturation on the properties of the final products (PU products).

## 2.2 EPOXIDATION OF UNSATURATED PLANT OILS

The project was initiated by investigating the epoxidation of (**2.11**), as the model plant oil, at various temperatures and in the absence and presence of air (oxygen), which was bubbled through the reactants mixture (Figure 2.4). A procedure previously published in the Clark group,<sup>79</sup> that of Coles *et al.* was chosen. A recent study investigating the epoxidation of oils using related tungstic acids<sup>94</sup> indicated that if oxygen was bubbled through the reaction mixture increased yields of epoxides could be produced. Therefore a study was conducted to investigate the effect of air bubbling through the reaction using our conditions. The temperature was also varied to determine the effect on the rate and yield of epoxidized rapeseed oil (**2.13**).

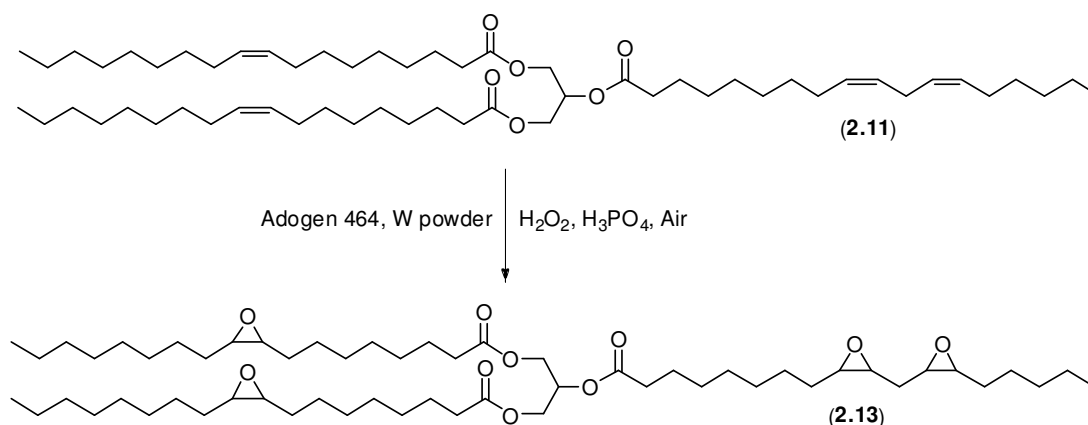


Figure 2.4 Epoxidation of (**2.11**)

Seven experiments were conducted in this study and are summarized in Table 2.2. The molar ratio between reactants and the experimental setup remained constant for these experiments. The duration of each experiment depended upon the time taken to fully convert the alkene ( $\delta = 5.35$  ppm) to epoxide functionality ( $\delta = 2.9$ -3.2 ppm), which was monitored by <sup>1</sup>H NMR.

The results of this study are represented in Figure 2.5, which is a line graph depicting the rate of conversion of the alkenes to epoxides against reaction time.

Table 2.2 Epoxidation of **(2.11)** with variation in reaction parameters.

Experiment (Exp.)	Reaction Temperature (°C)	Duration (hr)	Air or O <sub>2</sub> bubbling through reaction mixture	Yield of epoxidized product (%)
1	40	7	No	84
2	40	7	Air	82
3	40	7	O <sub>2</sub>	85
4	40	7	O <sub>2</sub> without H <sub>2</sub> O <sub>2</sub>	10
5	50	5	No	84
6	70	3	No	87
7	70	3	Air	85

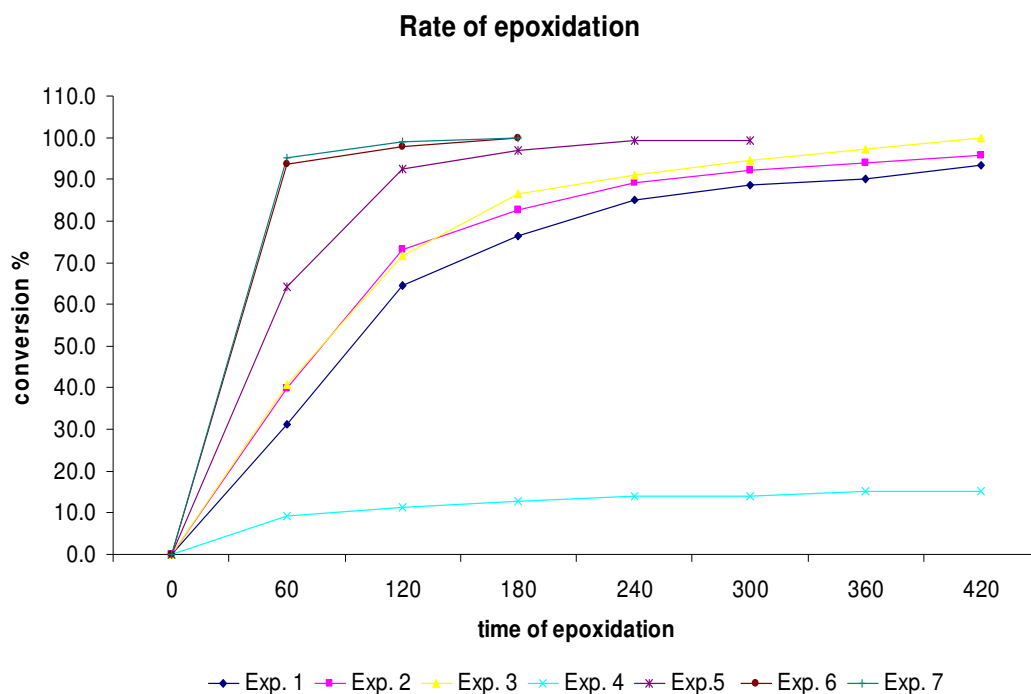


Figure 2.5 Rate of epoxidation for experiments conducted in Table 3

Both Experiment 1 and 2 were conducted at 40 °C; however, the main difference between these two experiments is that Experiment 2 had compressed air bubbled through the reaction mixture. Referring to Figure 2.5, the rate of epoxidation for Experiment 2 was slightly faster than Experiment 1 but not significantly different. This suggests that bubbling air (20% oxygen) through the reaction mixture helps to increase the rate of reaction only slightly. Nonetheless, both experiments needed 7 hours to achieve 93% and 96% conversion respectively for Experiment 1 and 2.

The epoxidation reaction was repeated with molecular oxygen (instead of air) bubbling through the reaction mixture (Experiment 3) and the rate of reaction increased slightly again as compared to the experiment conducted with compressed air (Experiment 2). This again suggests that the rate of epoxidation can be increased with a higher concentration of oxygen (molecular oxygen) in the reaction system. As a result, the alkene in Experiment 3 was fully reacted. As expected, the control reaction, where the epoxidation reaction was conducted with molecular oxygen bubbling through the reaction mixture but without hydrogen peroxide in the reaction system (Experiment 4), gave a very slow rate of epoxidation and the alkene conversion achieved after 7 hours reaction was only 15%.

Experiment 5 and 6 were conducted at 50 °C and 70 °C respectively to investigate the effect of temperature on the rate of reaction. As expected, the higher temperature increased the rate of conversion (at 50 °C; the conversion reached 99% after 4 hours of reaction and at 70 °C the conversion was completed after 2 hour). Experiment 6 was repeated with compressed air bubbling through the reaction mixture (Experiment 7) and the rate of epoxidation was not significantly different between Experiment 6

and 7. This suggests that at higher temperature (70°C), the rate of epoxidation was mainly influenced by temperature and not the concentration of oxygen in the reaction system.

Referring to Table 2.2, the yield of epoxidised rapeseed oil from these experiments is comparable to each other (except for Experiment 4), which is in the range of 82-87%, which means that the air bubbling and reaction temperature did not influence the yield of product but they do affect the rate of reaction.

### Properties of epoxidized products

The following Table 2.3 shows the properties of (2.13) prepared from these experiments.

Table 2.3 Properties of (2.13).

Experiment	Gel Permeation Chromatography			OOC (%)	OHV	AV
	% of Oligomer	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)			
1	3.0	3000	2700	5.20	15.6	1.49
2	3.5	2900	2700	5.34	16.8	1.51
3	3.8	2900	2700	5.40	16.3	1.50
4	0.2	2900	2700	0.75	2.4	1.50
5	4.0	3000	2700	5.98	16.8	1.51
6	1.75	2700	2600	5.71	11.3	1.51
7	1.7	2700	2600	5.73	11.0	1.50

OOC= oxirane oxygen content, OHV= hydroxyl value (mg KOH/g), AV= acid value (mg KOH/g)

Referring to Table 2.3, the results [% of oligomer, oxirane oxygen content (OOC%) and hydroxyl value (OHV)] for Experiment 4 are lower than other experiments due

to low alkene conversion and these values will not be used for comparison. The gel permeation chromatography analysis reveals that the epoxidation process produces mostly the desired epoxidized oils, however the process also produces about 1.7 – 4.0% oligomeric products and the average molecular weight of these products is about 3000 Da, which corresponds to dimers of triglycerides.

The acid value analysis indicates the level of free carboxylic acids in the mixture that will occur upon competitive hydrolysis of the triglycerides. The amount of free carboxylic acid groups remains fairly constant throughout the experiments (1.49 – 1.51) however the hydroxyl values (11 – 16.8) are significantly different. Hydroxyl groups come from two possible mechanisms (Figure 2.6) (1) ring opening of the epoxide with water to give a diol, (2) ring opening of the epoxide by a diol formed in mechanism (1), which leads to oligomerization. Thus it is no surprise that experiments 1-3 and 5 have similar levels of oligomerization and consequently hydroxyl values. Experiments 6 and 7 have lower percentage of oligomerization and consequently a lower hydroxyl value.

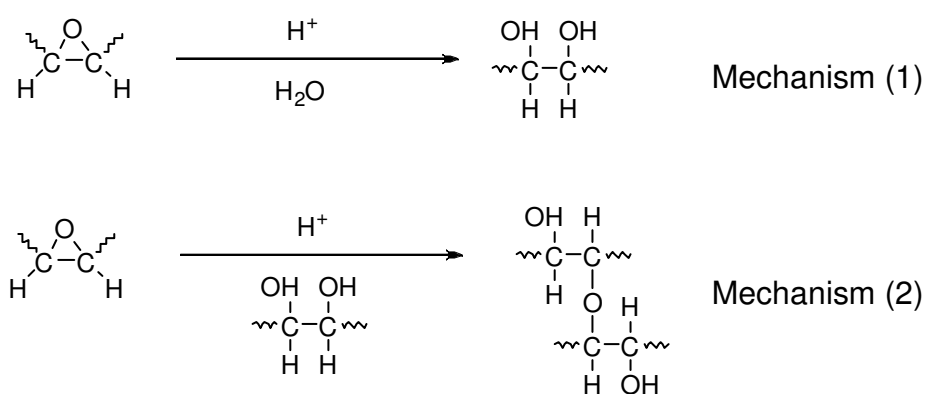


Figure 2.6 Mechanism of epoxide ring opening

The oxirane oxygen content (OOC) is a measurement of epoxy functionality and the reaction products show OOC% ranges from 5.2 to 6.0 with products from higher reaction temperature showing higher value. However, the theoretical value of OOC for 100% conversion is about 7.3%, indicating that the formed epoxy groups were converted to diols or the oligomerized triglyceride compounds.

The FTIR spectroscopy analysis of the epoxidized sample from Experiment 6 (Figure 2.7) confirmed the formation of the epoxy group, which shows an absorption at  $824\text{ cm}^{-1}$  and the alkene absorption at  $1650\text{ cm}^{-1}$  (C=C stretching vibration) and  $3000\text{ cm}^{-1}$  (alkene C-H stretching vibration) were not detected.  $^1\text{H}$  NMR spectroscopy was used to monitor the progress of the reaction by following the loss of alkene peak at 5.35 ppm and increase of peaks at 2.90-3.20 ppm, which correspond to the methine hydrogens of the epoxy group (Figure 2.8). While Figure 2.9 shows the high resolution mass spectrum of epoxidized rapeseed oil from Experiment 6.

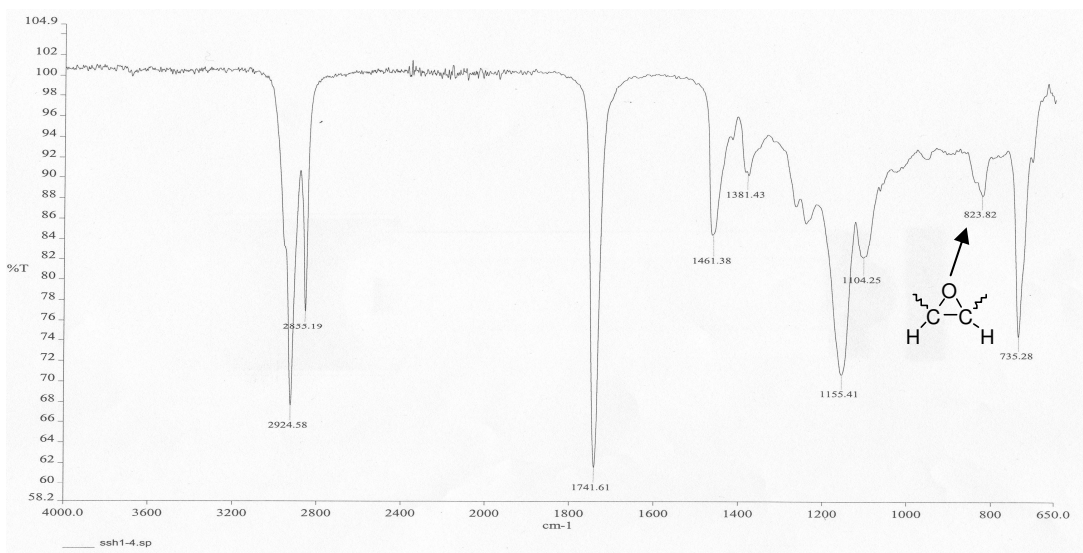


Figure 2.7 FTIR spectrum of (2.13)



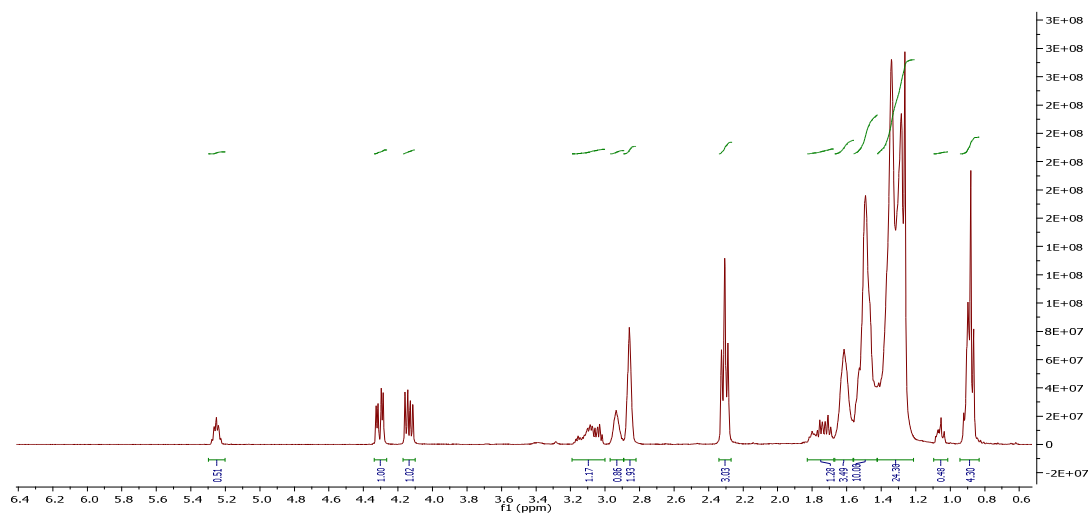


Figure 2.8 400 MHz  $^1\text{H}$  NMR spectrum of (**2.13**) in  $\text{CDCl}_3$

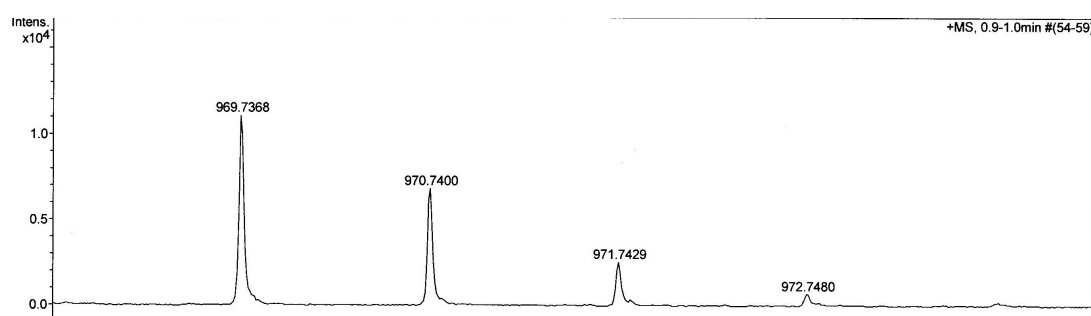


Figure 2.9 High resolution mass spectrum of (**2.13**) (ESI-HR-MS)

As a conclusion, based on results in Table 2.2, Table 2.3 and Figure 2.5, the reaction parameters of Experiment 6 was chosen as the general method for epoxidation of unsaturated plant oils because of the faster rate of reaction and less epoxide ring opened by-product.

### 2.3 COMPARISON BETWEEN TUNGSTEN POWDER CATALYST SYSTEM AND PEROXO PHOSPHOTUNGSTATE CATALYST SYSTEM IN THE EPOXIDATION OF METHYL OLEATE

The peroxo phosphotungstate catalyst ( $[(C_8H_{17})_3NCH_3]_3^+ [PO_4[W(O)(O_2)_2]_4]^{3-}$ ) was prepared according to method described by Venturello<sup>93</sup> *et al.* The peroxo phosphotungstate catalyst (PPT) system was used in the epoxidation of (**2.8**) as described by Poli<sup>94</sup> *et al.* The optimized reaction condition was conducted at 40 °C for 30 minutes with air bubbling through the reaction mixture to convert 97% of (**2.8**) to (**2.3**) (Figure 2.10).

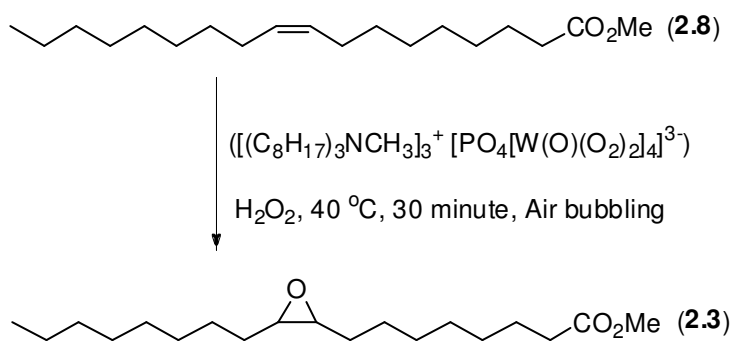


Figure 2.10 Epoxidation of (**2.8**) catalyzed by peroxo phosphotungstate system (PPT)

A study was conducted to find out whether the tungsten powder catalyst (TP) system developed by the Clark research group<sup>79</sup> was any better than the reported PPT system. Therefore, the epoxidation of (**2.8**) was conducted by using the optimized reaction parameters reported by Poli<sup>94</sup> *et al.* but the PPT was substituted with TP system (Figure 2.11).

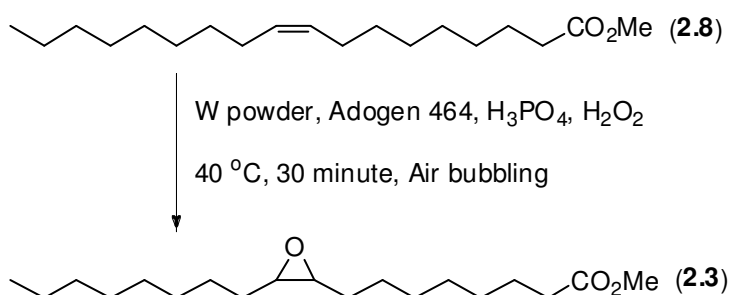


Figure 2.11 Epoxidation of (**2.8**) catalyzed by tungsten powder system (TP)

Furthermore, the epoxidation of (**2.8**) with the TP system was carried out at various temperatures to evaluate the effect of temperature on the yield of (**2.3**). The results of this study were tabulated in Table 2.4.

Table 2.4 Reaction parameters and properties of (**2.3**) from PPT and TP system

Entry	Catalyst system	Temperature (°C)	Yield (%)	AV	OHV	Oligomer (%)
1	TP	20	29	1.28	4.57	1.4
2	TP	30	44	1.29	6.04	2.1
3	TP	40	72	1.32	10.62	2.2
4	TP	60	83	1.34	24.28	3.6
5	PPT	40	87	7.92	13.65	0.0

OHV= hydroxyl value (mg KOH/g), AV= acid value (mg KOH/g)

<sup>1</sup>H NMR spectroscopy was used to measure the yield of (**2.3**) by measuring the integration of peaks at 2.9-3.2 ppm, which correspond to the methine hydrogens of the epoxy group.

Referring to Table 2.4, the optimized reaction conditions for the PPT system was repeated as Entry 5 and the reaction yielded 87% (**2.3**). When the PPT system was

substituted with TP system and varied the reaction temperature, the yield of **(2.3)** increases with the reaction temperature.

In comparison to the PPT system, the epoxidation reaction with TP system at 40 °C (Entry 3) and 60 °C (Entry 4) yielded 72% and 83% of **(2.3)** respectively, which were lower than the PPT system (Entry 5). This indicates that the PPT system is more efficient than the TP system that we have developed.

### Oligomers of (2.8)

In addition, the PPT system (Entry 5) did not produce any oligomers during the epoxidation reaction as analyzed by gel permeation chromatography (GPC). In contrast, epoxidation with TP system generated more oligomers of **(2.8)** (1%-3.6%, Entry 1 to 4) as the reaction temperature was increased. The oligomers were formed by epoxide ring opening by hydroxylated methyl oleate (**(2.14)**) during the epoxidation reaction according to mechanism shown below Figure 2.12.

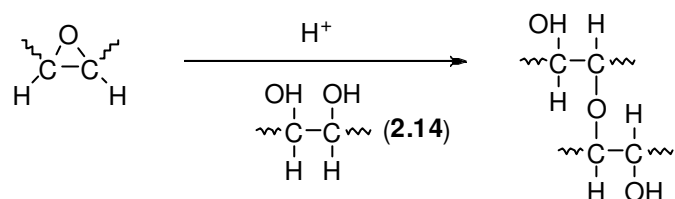


Figure 2.12 Mechanism of epoxide ring opening oligomerization of **(2.8)**

### Hydroxyl value

The oligomerization of **(2.8)** also produces hydroxyl functionality that can be analyzed by wet chemistry. Referring to Table 2.4, the hydroxyl value (a measure of hydroxyl functionality) increases with the reaction temperature, which corresponds to the amount of oligomers formed respectively to reaction temperature (Entry 1 to 4).

However, the PPT system (Entry 5) also produces hydroxyl functionality even though it did not produced oligomers. The hydroxyl functionality came from epoxide ring opening by water as shown in Figure 2.13, which produces (2.14).

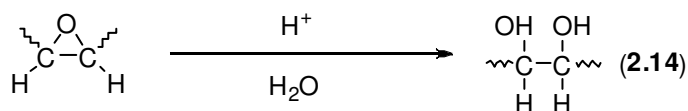


Figure 2.13. Epoxide ring opening by water to yield (2.14)

### Acid Value

The epoxidation reaction with the PPT system (Entry 5) produces higher acid value (7.92 mg KOH/g) as compared to TP system (1.28-1.34 mg KOH/g, Entry 1 to 4) indicating that the PPT system produces more carboxylic group (hydrolysis) during epoxidation as compared to TP system,(Figure 2.14). The results in Table 2.4 also show that for TP system (Entry 1 to 4), the reaction temperature has little effect on hydrolysis of the ester group of (2.8).

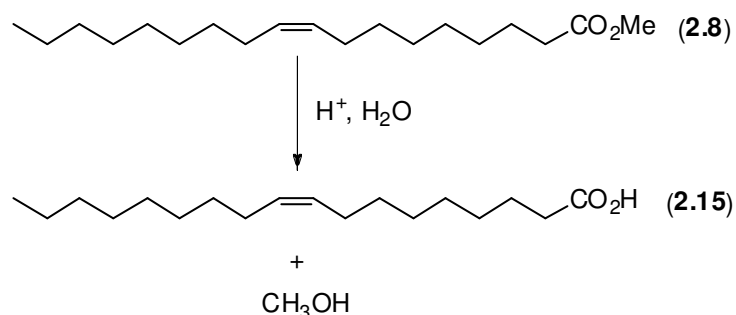


Figure 2.14 Hydrolysis of (2.8) to (2.15) and methanol during epoxidation

In summary, even though the PPT system is more efficient for the epoxidation of methyl oleate compared to the TP system, the significant hydrolysis of the ester group (side reaction), made the system unsuitable for the epoxidation of unsaturated

plant oils in this study because it would not be compatible with the aim of making oligomeric polyols from the epoxidized oil

The other side reaction (oligomerization) found in the TP system, is acceptable because in the later part of the study was aimed at making oligomeric polyols from the epoxidized oil. Therefore, the TP system was chosen as the method to epoxidize unsaturated plant oil throughout this study.

## 2.4 EPOXIDATION OF PLANT OILS

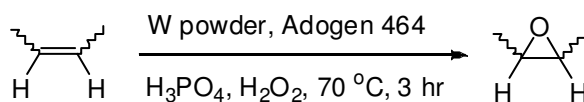


Figure 2.15 Epoxidation of unsaturated plant oil

For the purpose of this study, five plant oils were epoxidized with hydrogen peroxide by using the tungsten powder catalyst system (TP) (Figure 2.15). The prepared epoxidized plant oils (Figure 2.16) were epoxidized methyl oleate (**EMO**, **2.3**), epoxidized cocoa butter (**ECB**, **2.16**), epoxidized palm oil (**EPO**, **2.17**), epoxidized rapeseed oil (**ERO**, **2.13**) and epoxidized soybean oil (**ESO**, **2.6**).

The yield and oligomeric content of the epoxidized plant oils was determined by GPC and  $^1\text{H}$  NMR analysis. The most abundant epoxidized plant oil structure for respective plant oils (Figure 2.16) was determined by high resolution mass spectrometry (HRMS) and  $^1\text{H}$  NMR. The properties of these epoxidized oils are tabulated in Table 2.5.

The different level of epoxide functionality of the respective plant oils enables the study on the effect of plant oils structure/unsaturation on the properties of the oligomeric polyols as well as the final products (polyurethane products).

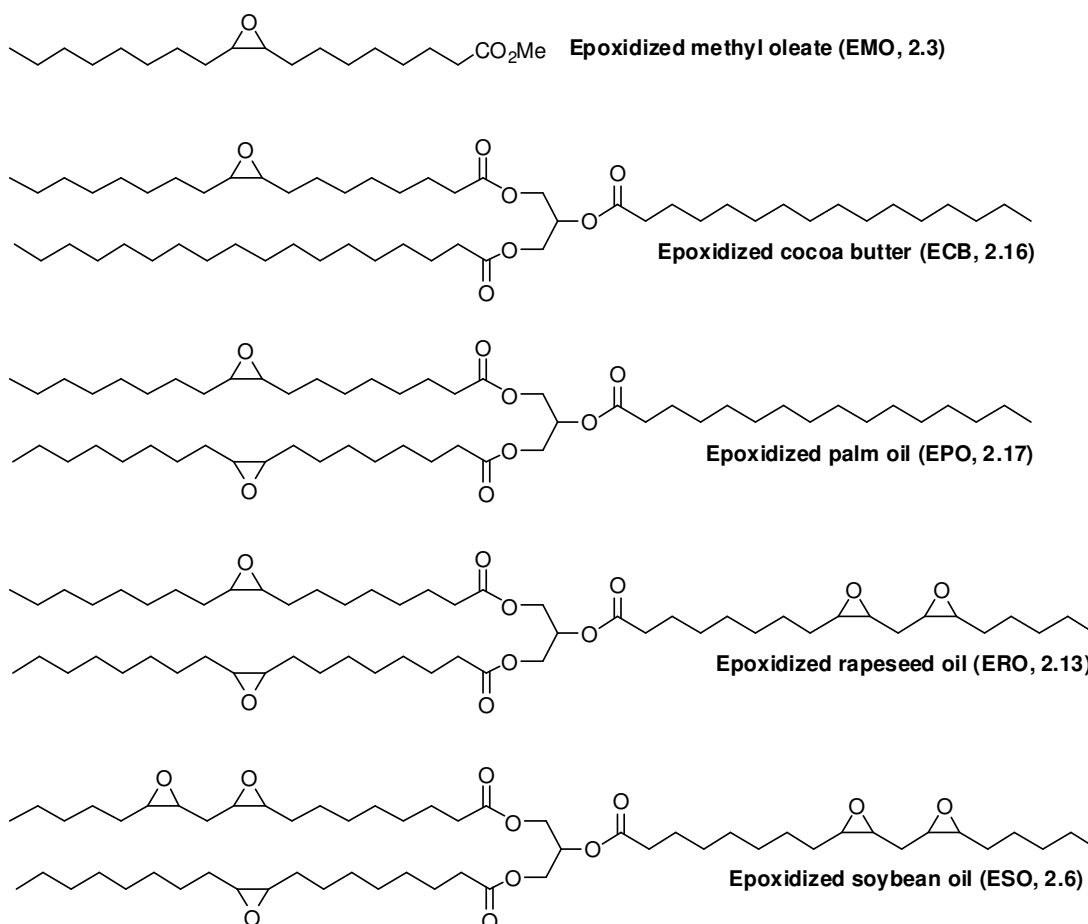


Figure 2.16 Epoxidized plant oils

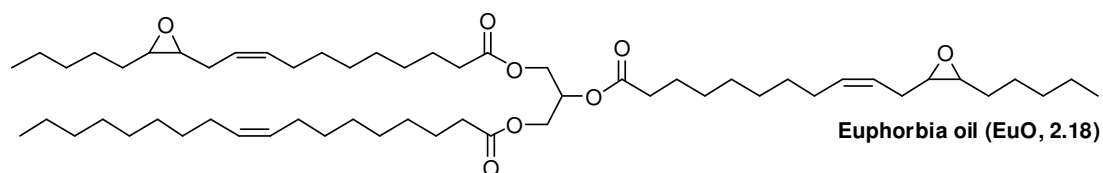
Table 2.5 Properties of the epoxidized oil

Epoxidized oil	Yield (%)	Oligomers (%)	OHV	AV
(2.3)	92	7	26	2.1
(2.16)	93	6	21	3.2
(2.17)	95	3	19	1.5
(2.13)	93	2	16	1.8
(2.6)	91	7	23	2.3

OHV= hydroxyl value (mg KOH/g), AV= acid value (mg KOH/g)

The results in Table 2.5 shows that the yield of epoxidized plant oils from the tungsten powder catalyzed epoxidation reaction were good. As expected the epoxidation reaction generated some oligomers of plant oil through epoxide ring opening, which give rise to a significant hydroxyl value. There is also a small degree of hydrolysis but in general, the properties of the epoxidized plant oils are acceptable for use in making oligomeric polyols for our purposes.

At this point of the research, a plant oil extracted from *Euphorbia lagacae* seed that naturally contains an epoxide functionality and alkene (unsaturation) was also included as one of the starting material in this study. The plant oil was analyzed by ESI mass spectrometry and  $^1\text{H}$  NMR spectroscopy to reveal the most abundant triglycerides as shown in Figure 2.17. For the purpose of discussion, this plant oil shall be known as euphorbia oil (**EuO**, **2.18**).

Figure 2.17 Structure of the most abundant triglycerides in (**2.18**)



## 2.5 OLIGOMERIZATION OF EPOXIDIZED PLANT OILS BY EPOXIDE RING OPENING WITHOUT SOLVENT

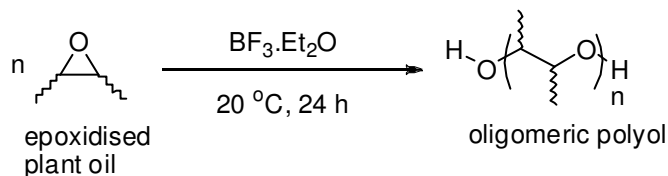


Figure 2.18 Oligomerization of epoxidized plant oils without solvent

The prepared epoxidized plant oils from section 2.4 were used as starting materials for the synthesis of oligomeric polyols. In the first approach, the epoxidized plant oils were oligomerized with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as the catalyst without solvent at  $20\text{ }^{\circ}\text{C}$  to yield oligomeric polyols (Figure 2.18). The yields of the oligomeric polyols were determined by GPC and  $^1\text{H}$  NMR analysis. The following are the properties of products tabulated in Table 2.6.

Table 2.6 Properties of oligomeric polyols from ring opened epoxidized oil

Epoxidised oil	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
(2.3)	0.15	76	2000	1800	1.11
(2.16)	0.15	56	6700	6100	1.10
(2.17)	0.15	Gelled	-	-	-
(2.13)	0.15	Gelled	-	-	-
(2.6)	0.15	Gelled	-	-	-
(2.18)	0.15	Gelled	-	-	-

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

The ring opening of **(2.17)**, **(2.13)**, **(2.6)** and **(2.18)** with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  resulted in cross-linked (gelled) polymers which were soft gel solids at room temperature, while **(2.3)** and **(2.16)** yielded 76% and 56% oligomeric polyols respectively. The epoxidized oils **(2.17)**, **(2.13)**, **(2.6)** and **(2.18)** have more than one epoxy group per molecule compared to epoxidized oils **(2.3)** and **(2.16)** and this multiple epoxy group enables them to form cross-linked polymer. These cross-linked polymers were not soluble in common solvents such as hexane, toluene, diethyl ether, dichloromethane, chloroform, tetrahydrofuran, methanol, dimethylformamide and dimethyl sulfoxide. Therefore, no further analysis was performed on them.

It is proposed that the oligomerization of epoxidized oil occurs through the mechanism illustrated in Figure 2.19, where the initiation step involves the activations of the epoxide group by ion complex of  $\text{BF}_3$  **(2.19)**, where **(2.19)** was formed from the reaction between  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and trace water found in the epoxidized oils.

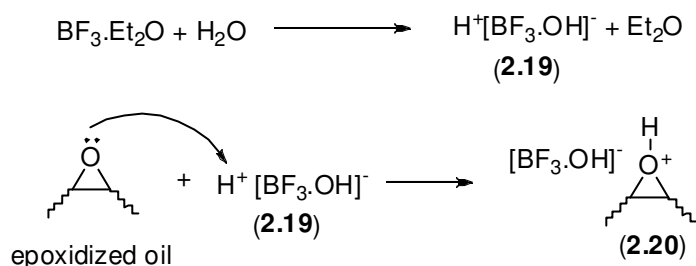


Figure 2.19 Initiation of epoxide ring opening oligomerization

The propagation step involves the nucleophilic attack of the activated epoxide group **(2.20)** by epoxide group from another molecule of plant oil (Figure 2.20). This process regenerates **(2.20)** for another nucleophilic attack and propagates the polymerization reaction. Termination step involves the nucleophilic attack of **(2.20)**

by water to generate oligomeric polyol with hydroxyl functionality (2.21) (Figure 2.21).

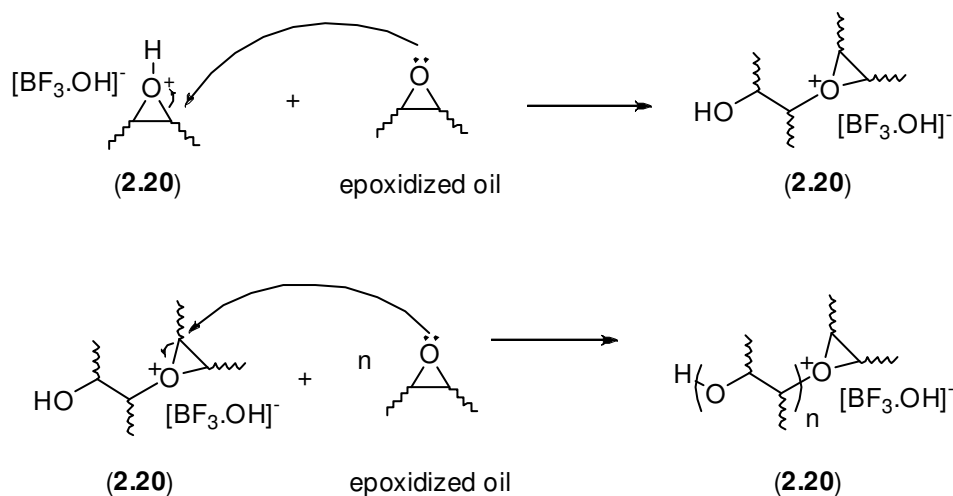


Figure 2.20 Propagation step in epoxide ring opening oligomerization

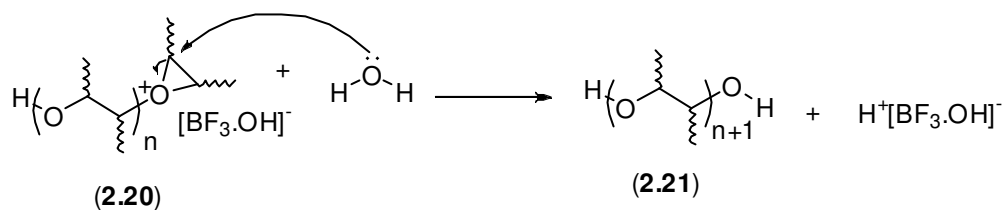


Figure 2.21 Termination step in epoxide ring opening oligomerization

In order to produce non-cross-linked polyols from **all** the epoxidized oils, the oligomerization reaction was conducted in solvents (instead of bulk) and with lower amount of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (catalyst). The effect of solvent is to reduce the concentration of monomer, which helps to reduce the chances of the cross-linking between propagating chains. The lower amount of catalyst also reduces the initiation reaction which in turn reduces the amount of propagating chain, which helps to reduce the chances of cross-linking between propagating chains.

## 2.6 RING OPENING OF EPOXIDIZED METHYL OLEATE IN SOLVENT

The **(2.3)** was oligomerized in hexane with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as the catalyst without ring opening agent at room temperature to yield oligomeric polyols **(2.22)** (Figure 2.22).

The following are the properties of **(2.22)** tabulated in Table 2.7.

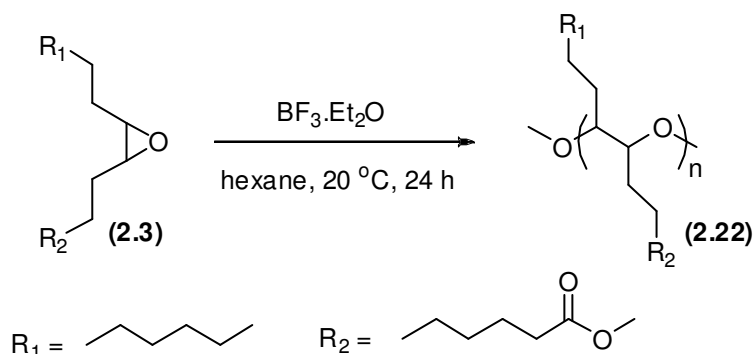


Figure 2.22 Ring opening oligomerization of **(2.3)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Table 2.7 Properties of **(2.22)** from ring opened **(2.3)**

Entry	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.03	57	1500	860	1.74
2	0.05	85	1800	1500	1.20
3	0.10	85	2100	1900	1.10

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

The reaction was able to achieve good yield (85%) of **(2.22)** from **(2.3)** by using 0.05 mol of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  per mol of epoxy group (Entry 1). Similar result was achieved when higher amount of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.1 mol equivalent) was used (Entry 2). When lower amounts of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  were used (0.03 mol equivalent), the yield of **(2.22)** dropped to 57% (Entry 3).

When compared to ring opening of (**2.3**) without solvent (refer to Table 2.6, (**2.3**)), the same reaction (epoxy ring opening with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) carried out with solvent gave a better yield (85% vs 76%) even with lower amount of catalyst (0.05 mol Vs 0.15 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  respectively).

High resolution mass spectrometry (HRMS) analysis shows that the (**2.22**) has an average molecular weight of 977 Da, which corresponded to the sodium adduct of the trimer of (**2.3**) formed by an ether linkage (Figure 2.23). The repeating unit of the oligomers has a molecular weight of 312 Da.

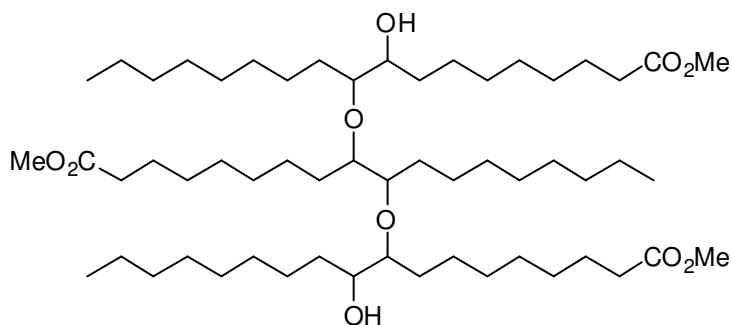


Figure 2.23 Trimer of (**2.3**)

Gel permeation chromatography (GPC) results need to be treated with caution as the instrumentation was calibrated for analysis of polymethacrylate polymers. However, the GPC of the monomer (**2.3**) was ran as a standard. This indicated a number average molecular weight of about 500 Da. A GPC of the ring opened (**2.22**) was mainly a trimer based upon this standard with a number average molecular weight of about 1500 Da (Table 2.7 , Entry 2).

The following Figure 2.24 shows the stacked  $^1\text{H}$  NMR spectrum of (**2.3**) and (**2.22**) prepared from it. Referring to the  $^1\text{H}$  NMR spectrum, the epoxide group of (**2.3**) at

2.86-3.14 ppm was ring opened to yield ether and hydroxyl functionalities (3.20-3.60 ppm) of the **(2.22)**.

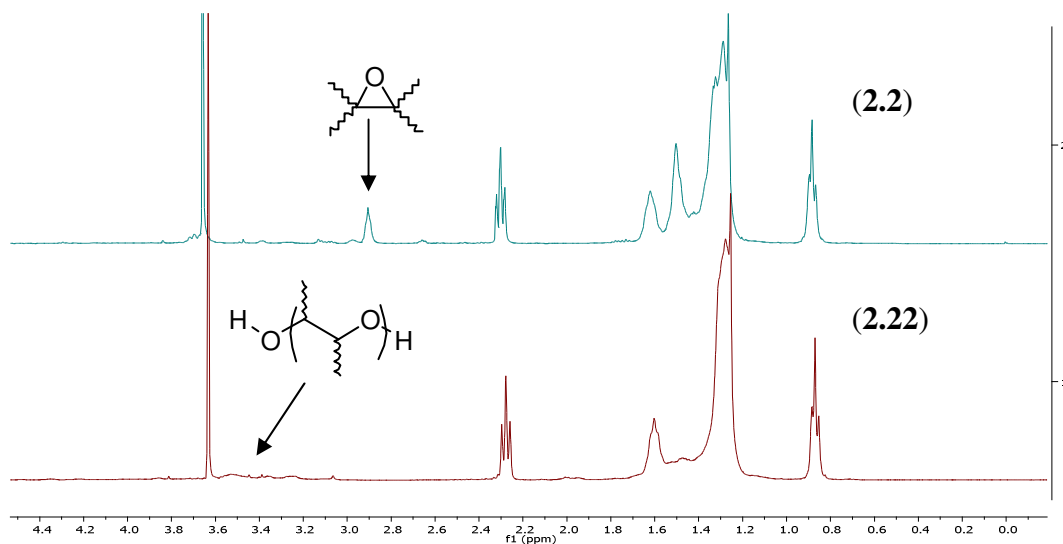


Figure 2.24 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of **(2.3)** and **(2.22)** in  $\text{CDCl}_3$

## 2.7 RING OPENING OF EPOXIDIZED COCOA BUTTER IN SOLVENT

The oligomerization of epoxidized cocoa butter **(2.16)** was catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  without ring opening agent in hexane at room temperature to yield oligomeric polyols **(2.23)** (Figure 2.25). The properties of **(2.23)** are tabulated in Table 2.8.

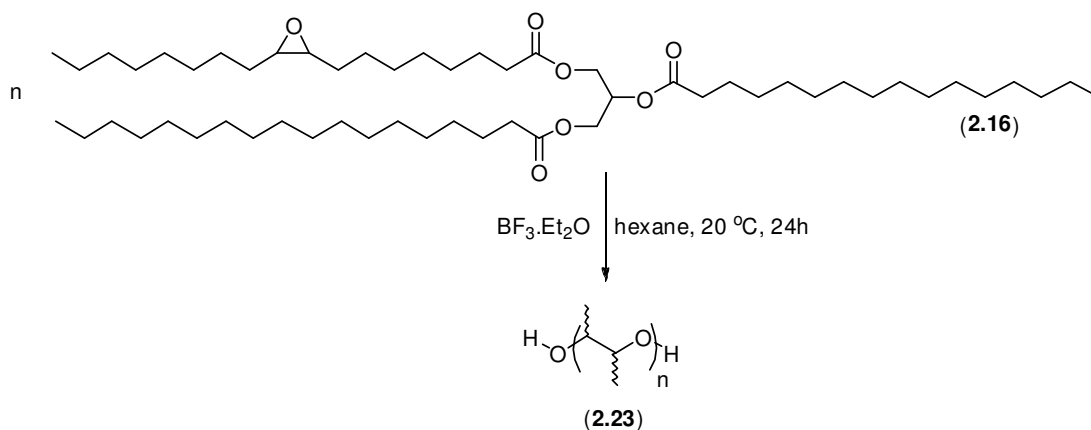


Figure 2.25 Ring opening oligomerization of **(2.16)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Table 2.8 Properties of **(2.23)** from ring opened **(2.16)**

Entry	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.03	19	6200	5700	1.09
2	0.05	49	6800	5900	1.15
3	0.10	87	8400	7300	1.15

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

The ring opening of **(2.16)** with 0.1 mol equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  per mol of epoxy group gave reasonable yields of **(2.23)** (87%) (Entry 3), but dropped significantly at lower catalyst loadings (Entry 1 & 2). When compared to ring opening of ECB without solvent (Table 2.4, **(2.16)**), the yield were better even with a lower amount of catalyst (0.1 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (87% vs 56%).

GPC analysis of monomer **(2.16)** (as a standard ~ 1000 Da) gave a  $M_n$  = 1500 Da. Referring to Table 2.8 (Entry 3), the GPC analysis shows that the **(2.23)** has a  $M_n$  =

7300 Da. Therefore, a conclusion can be made that the oligomeric polyols made from **(2.16)** had on average 5 units of **(2.16)** linked together by the ether functionality.

Matrix assisted laser desorption/ionization time-of flight (MALDI-TOF) mass spectrometry (MS) analysis confirmed oligomerization with dimers, trimers and tetramers of **(2.16)** (Figure 2.26) . Figure 2.26 shows the tetramer ( $\text{Na}^+$  adduct peak of 3577 Da) and the repeating unit of 877 Da as shown in Figure 2.27.

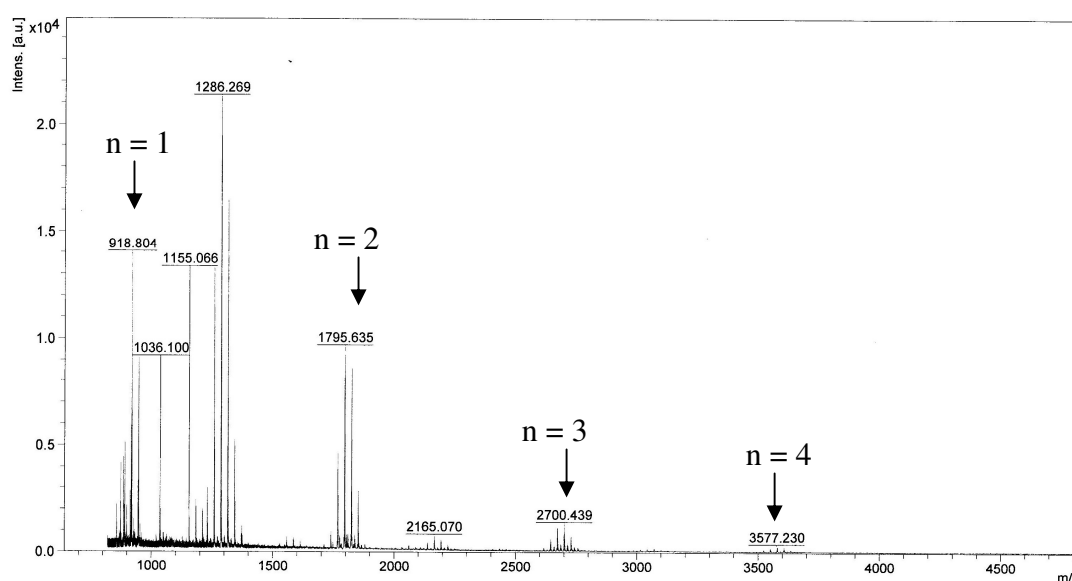


Figure 2.26 MALDI-TOF-MS spectrum of **(2.23)** by using 2,5-dihydroxy benzoic acid (DHB) as the matrix in the analysis

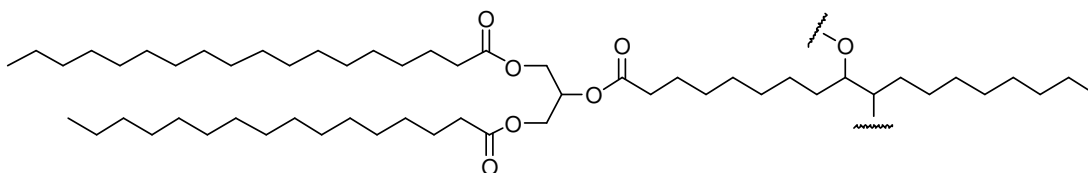


Figure 2.27 Repeating unit in oligomers of **(2.23)**



Figure 2.28 shows the stacked 400 MHz  $^1\text{H}$  NMR spectrum of **(2.16)** and **(2.23)** in  $\text{CDCl}_3$ . Referring to the  $^1\text{H}$  NMR spectrum, the epoxide group of **(2.16)** at 2.78-3.05 ppm was ring opened to yield ether and hydroxyl functionalities (3.10-3.65 ppm) of the **(2.23)**.

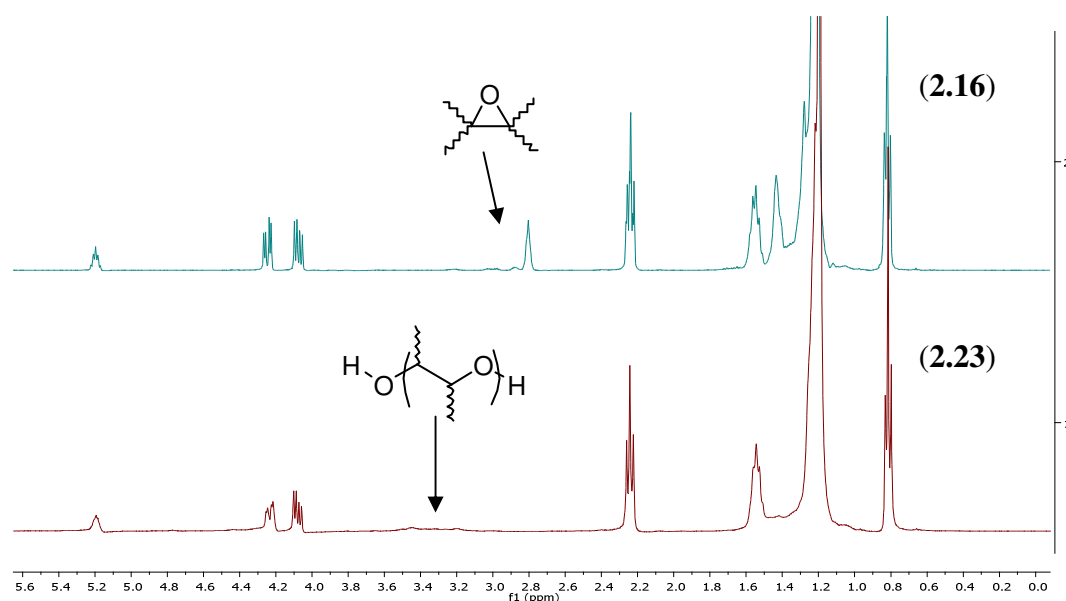


Figure 2.28 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of **(2.16)** and **(2.23)** in  $\text{CDCl}_3$

## 2.8 RING OPENING OF EPOXIDIZED PALM OIL IN SOLVENT

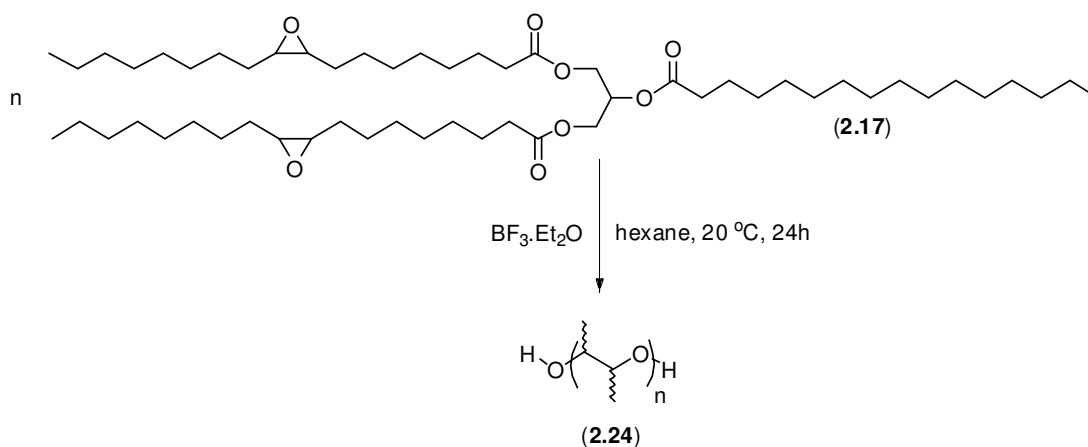


Figure 2.29 Ring opening of **(2.17)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

The oligomerization of **(2.17)** was conducted in the same way as **(2.16)** (Figure 2.29) and the products were analyzed by GPC and  $^1\text{H}$  NMR as before.

Table 2.9 Properties of **(2.24)** from ring opened **(2.17)**

Entry	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.0325	85	226000	24000	9.41
2	0.0350	90	470000	27000	17.3
3	0.0375	Gelled	-	-	-

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

When epoxide ring opening reaction of **(2.17)** was conducted without solvent (refer to page 71, Table 2.6, **(2.17)**), the product was cross-linked (gelled) polymer. When the same ring opening reaction was conducted in solvent (*n*-hexane) with lower amount of catalyst (0.0375 mol equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (Table 2.9, Entry 3), gelled polymer was produced. However, when the reaction was conducted with even lower amount of catalyst (0.035 mol equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (Entry 2), a liquid **(2.24)** was obtained in good yield (90%). When the amount of catalyst was further lowered (0.0325 mol equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (Entry 1), the yield (85%) as well as the average molecular weight of the EPOP was even lower. This indicated that the reaction parameters (catalyst amount, monomer concentration, temperature, duration) reaction could be manipulated to influence the molecular weight and yield of the oligomeric polyols.

## 2.9 EFFECT OF MONOMER CONCENTRATION ON THE PROPERTIES OF OLIGOMERIC POLYOL

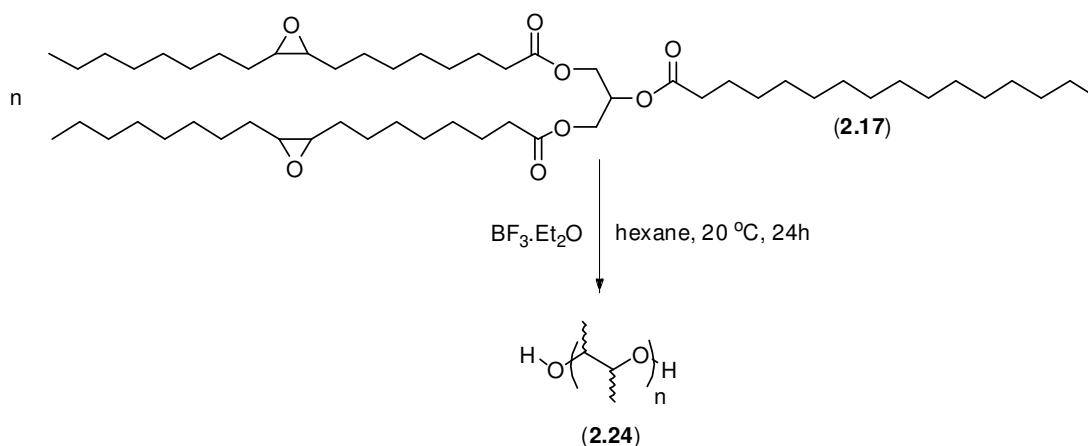


Figure 2.30 Ring opening of **(2.17)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

For this study, **(2.17)** was used as the starting material for epoxide ring opening oligomerization (Figure 2.30). The concentration of the monomer used in the ring opening reaction was varied in order to observe changes in the properties of the **(2.24)**. The following Table 2.10 displays the properties of products from this study.

Table 2.10 Properties of **(2.24)** from ring opened **(2.17)** on different concentration

Entry	Concentration ( $\times 10^{-4}$ mol/ml)	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
				$M_w$ (Da)	$M_n$ (Da)	PDI
1	3.75	0.0375	Gelled	-	-	-
2	1.87	0.0375	89	82600	18500	4.47
3	3.75	0.0350	90	467000	27000	17.3
4	1.87	0.0350	85	58200	16100	3.61

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

When the epoxide ring opening oligomerization reaction was conducted at concentration  $3.75 \times 10^{-4}$  mol/ml and 0.0375 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (Entry 1), the product was a cross-linked (gelled) polymer. However, when the reaction was repeated at lower concentration ( $1.87 \times 10^{-4}$  mol/ml) (Entry 2), the product was liquid **(2.24)** (89% yield) with number average molecular weight ( $M_n$ ) of 18500 Da.

When the same comparison was made ( $3.75 \times 10^{-4}$  mol/ml vs  $1.87 \times 10^{-4}$  mol/ml) with a lower amount of catalyst (0.035 mol equivalent  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (Entry 3 and 4), the yield of product was similar (90% vs 89%) but the average molecular weight of **(2.24)** from  $1.87 \times 10^{-4}$  mol/ml reaction (Entry 4) was lower and the PDI was narrower than polyol from  $3.75 \times 10^{-4}$  mol/ml (Entry 3). Thus, higher concentrations lead to larger molecular weights and more cross-linking and larger PDI's.

## **2.10 EFFECT OF REACTION TEMPERATURE ON THE PROPERTIES OF OLIGOMERIC POLYOL**

The epoxide ring opening oligomerization reaction of **(2.17)** was repeated at different temperatures to evaluate the effect of temperature on the properties of **(2.24)**. The following Table 2.11 tabulates the result of this study.

Table 2.11 Properties of **(2.24)** from ring opened **(2.17)** at different temperature

Entry	Temperature (°C)	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
				M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	20	0.0375	Gelled	-	-	-
2	60	0.0375	86	151000	18500	8.16
3	20	0.0350	90	467000	27100	17.3
4	60	0.0350	83	62600	17500	3.58

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

When the reaction was conducted at 20 °C with 0.0375 mol equivalent of BF<sub>3</sub>.Et<sub>2</sub>O (Entry 1), the product was a cross-linked (gelled) polymer. However, by rising the reaction temperature to 60 °C (Entry 2), the product was a liquid **(2.24)** (86% yield) with an average molecular weight (M<sub>n</sub>) of 18500 Da.

When reactions were conducted with lower amount of catalyst (0.035 mol equivalent of BF<sub>3</sub>.Et<sub>2</sub>O) at 20 °C (Entry 3) and 60 °C (Entry 4), the **(2.24)** from 60 °C has lower average molecular weight and narrower PDI. Therefore, it is apparent higher reaction temperature promotes chain termination during oligomerization resulting in smaller molecular weights and narrower molecular weight distribution.

## 2.11 THE EXTENT OF EPOXIDE RING OPENING OLIGOMERIZATION REACTION AGAINST TIME

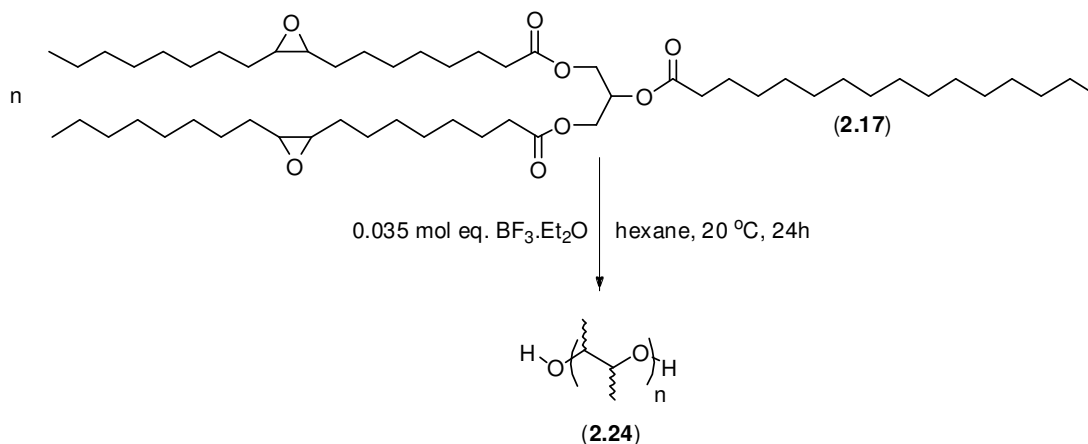


Figure 2.31 Ring opening of **(2.17)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

A study was conducted to evaluate the extent of epoxide ring opening oligomerization reaction of **(2.17)** catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  against time (Figure 2.31). A small aliquot was removed from the reaction mixture after 30 minutes of reaction and then at every hour of reaction. The small sample was washed with water to quench the reaction before analyzing it with GPC. The following Table 2.12 shows the result of this study.

Table 2.12 The extent of epoxide ring opening oligomerization reaction of **(2.17)** catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  against time

Reaction time (hr)	Oligomeric content (%)	Gel permeation chromatography		
		$M_w$ (Da)	$M_n$ (Da)	PDI
0.5	82	37900	13200	2.89
1	84	43200	13800	3.14
2	86	47100	14500	3.25
4	88	49800	14900	3.34
6	89	58100	15300	3.78
8	90	61600	16000	3.85
12	91	64500	16300	3.94
24	93	76300	17800	4.30

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

Referring to Table 2.12, the oligomeric content of the reaction mixture reached 82% by the first 30 minutes of the reaction, which means that the epoxy ring opening oligomerization reaction happened rapidly as soon as the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was added to the reaction mixture. It took a further 24 hours to increase the oligomeric content to 93% and at the same time the PDI of the product also broadens indicating more polymer chains are cross-linking with the longer reaction time. Referring to Table 2.12, the  $M_n$  of **(2.24)** was 17800 Da, which correspond to about 12 units of **(2.17)** linked by an ether functionality (taking one unit of **(2.17)** as 1500 Da as analyzed by GPC).

As before the MALDI-TOF-MS analysis (Figure 2.32) showed oligomers upto the tetramer (sodium adduct peak of 3562 Da) and a repeating unit of 890 Da (Figure 2.33). The higher oligomers were not detected by MALDI-TOF-MS due to detector saturation caused by continuous stream of particles impacting the detector causes a loss of sensitivity at higher molecular masses.

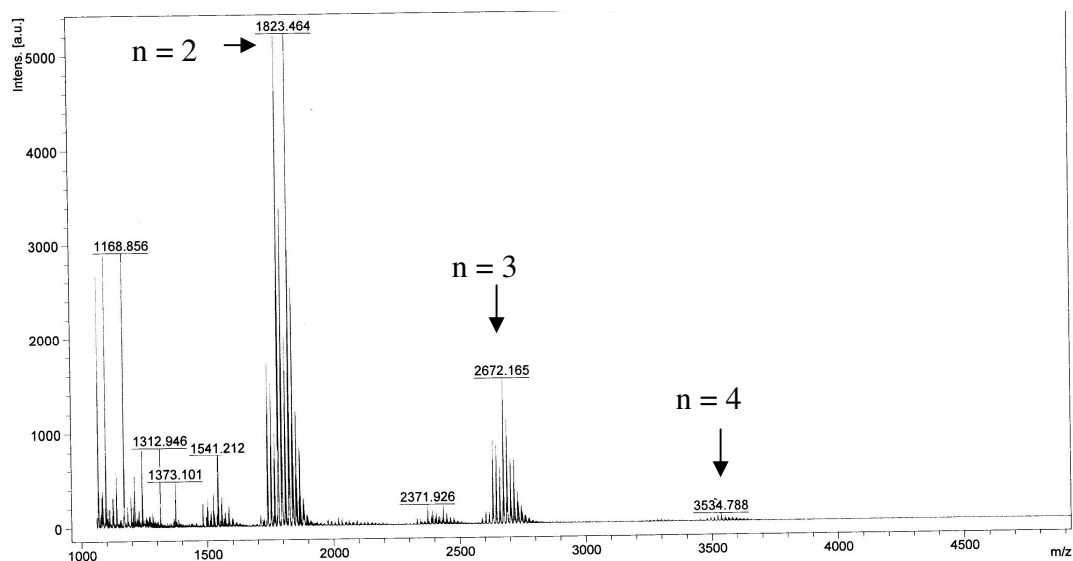


Figure 2.32 MALDI-TOF-MS spectrum of **(2.24)** by using DHB as the matrix in the analysis

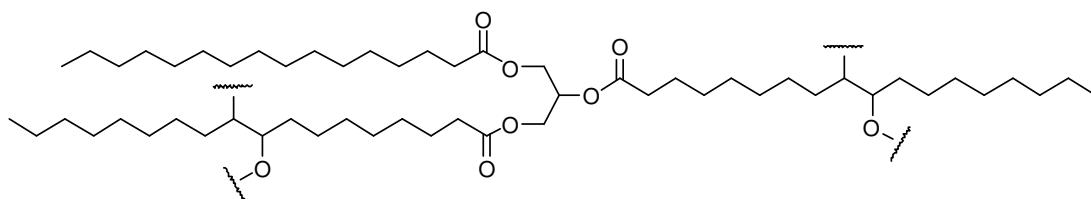


Figure 2.33 Repeating unit in oligomers of **(2.24)**

The reaction was also followed by  $^1\text{H}$  NMR analysis and the following Figure 2.34 shows the stacked  $^1\text{H}$  NMR spectrum of **(2.17)** at 30 minute, 6 hours, 12 hours and 24 hours of reaction time.  $^1\text{H}$  NMR analysis shows that the epoxide group of **(2.17)** (2.80-3.10 ppm) was ring opened to ether and hydroxyl functionality (3.30-3.65 ppm) as shown in Figure 2.34.



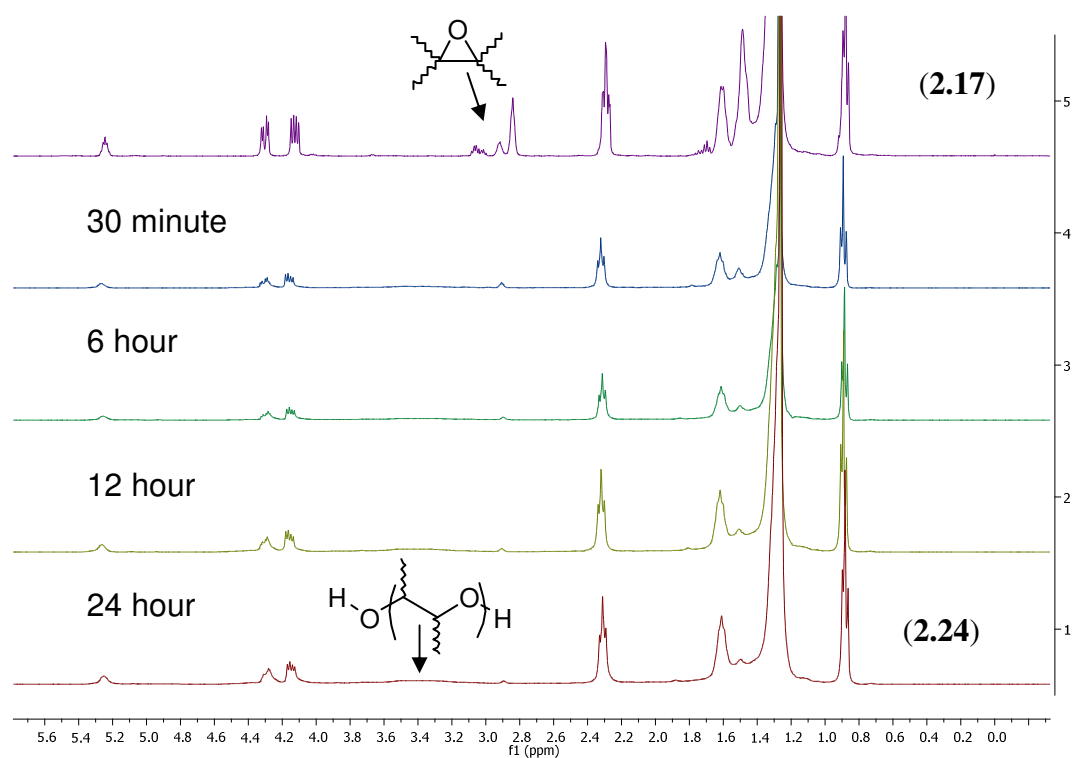


Figure 2.34 Stacked 400 MHz  $^1\text{H}$  NMR of **(2.17)** and reaction mixture at certain reaction time in  $\text{CDCl}_3$

## 2.12 RING OPENING OF EPOXIDIZED RAPESEED OIL IN SOLVENT

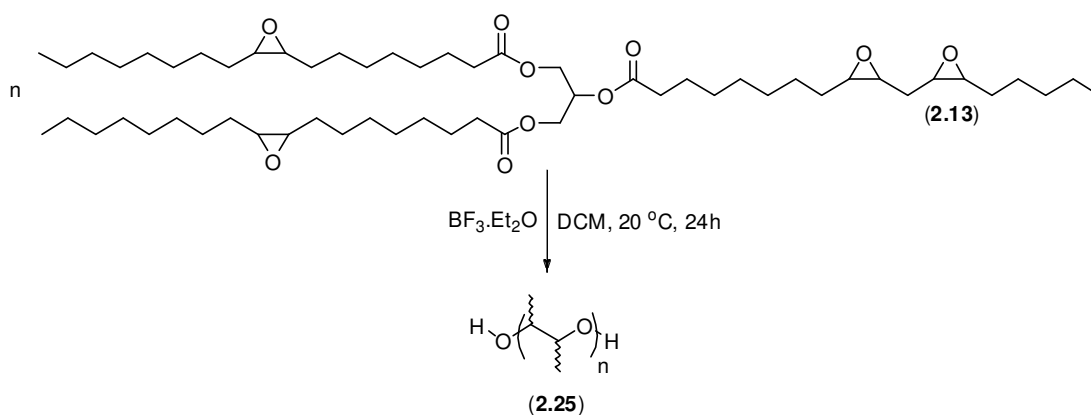


Figure 2.35 Ring opening of **(2.13)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

The oligomerization of epoxidized rapeseed oil (**2.13**) was catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  without ring opening agent at room temperature to yield (**2.25**). The reaction was conducted in anhydrous dichloromethane (DCM) instead of *n*-hexane because (**2.13**) did not dissolve completely in *n*-hexane (Figure 2.35). The reaction products were analyzed by  $^1\text{H}$  NMR and GPC as before. The following are the properties of products tabulated in Table 2.13.

Table 2.13 Properties of (**2.25**) from ring opened (**2.13**)

Entry	Concentration ( $\times 10^{-4}$ mol/ml)	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
				$M_w$ (Da)	$M_n$ (Da)	PDI
1	3.52	0.03	Gelled	-	-	-
2	1.76	0.03	77	110000	9200	11.5
3	1.76	0.0275	77	24800	9700	2.55

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

When the epoxide ring opening reaction was conducted with  $3.52 \times 10^{-4}$  mol/ml of monomer concentration and 0.03 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (Entry 1), the product was cross-linked (gelled) polymer. However, when the same reaction was repeated with more solvent ( $1.76 \times 10^{-4}$  mol/ml, Entry 2), the product was a liquid oligomeric polyol (77 % yield) with average molecular weight ( $M_n$ ) of 9200 Da.

GPC analysis reveals that the (**2.25**) has  $M_n = 9700$  Da, which corresponds to oligomers of 6 units of (**2.13**) linked by ether functionality (one unit of (**2.13**) is about 1500 Da as analyzed by GPC). MALDI-TOF-MS analysis (Figure 2.36) shows that (**2.25**) contains tetramer ( $n=4$ ) of (**2.13**) (Figure 2.36) with a repeating unit of 980 Da represented by Figure 2.37.

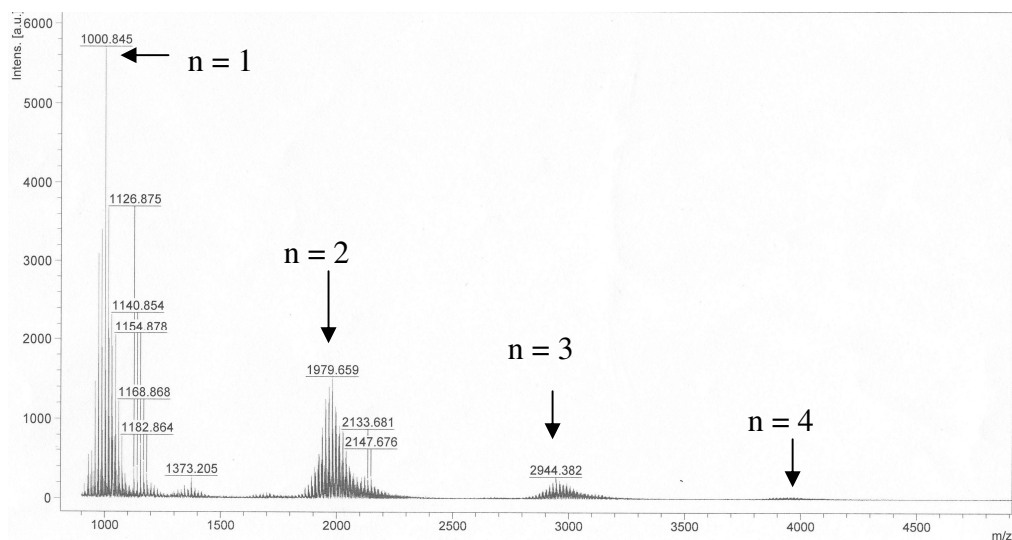


Figure 2.36 MALDI-TOF-MS spectrum of **(2.25)** by using DHB as the matrix in analysis

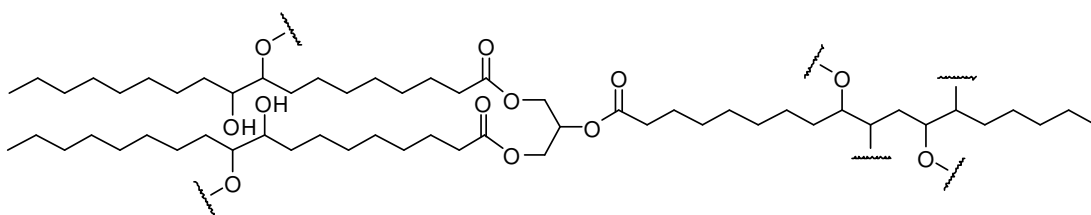


Figure 2.37 Repeating unit in **(2.25)**

### 2.13 RING OPENING OF EPOXIDIZED SOYBEAN OIL IN SOLVENT

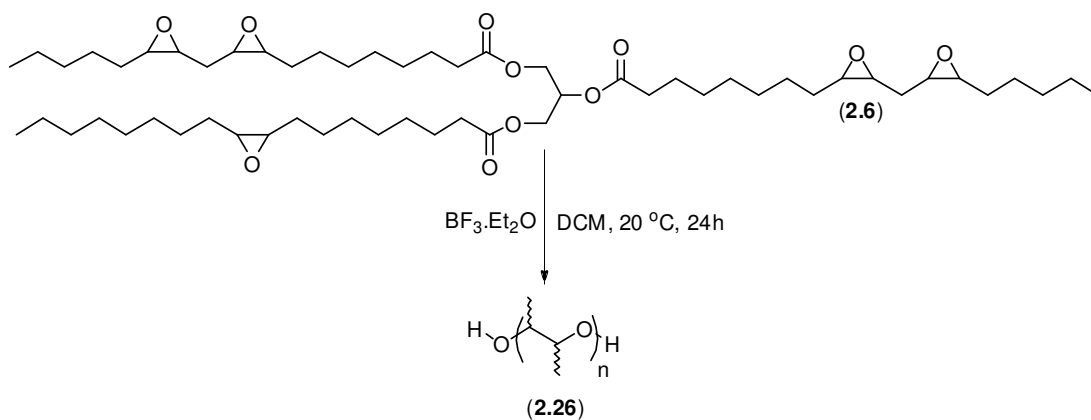


Figure 2.38 Ring opening of **(2.6)** in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

The oligomerization of epoxidized soybean oil (**2.6**) was conducted in similar method as (**2.13**) (Figure 2.38). The following are the properties of products tabulated in Table 2.14.

Table 2.14 Properties of products from ring opened (**2.6**)

Entry	Concentration (x 10 <sup>-4</sup> mol/ml)	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
				M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	3.47	0.0325	Gelled	-	-	-
2	3.47	0.03125	74	50800	17200	2.94
3	1.74	0.03375	87	1030000	15800	65.1
4	1.04	0.03375	82	147000	9600	15.3

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

GPC analysis shows that the (**2.26**) has an average molecular weight of about 9600 Da, which corresponds to hexamer of (**2.6**) linked by an ether functionality (one unit of (**2.6**) is about 1500 Da as analyzed by GPC). MALDI-TOF-MS analysis of (**2.26**) shows that the oligomeric polyols contain up to tetramer (n=4) of (**2.6**) (Figure 2.39) with a repeating unit of 994 Da represented by Figure 2.40.

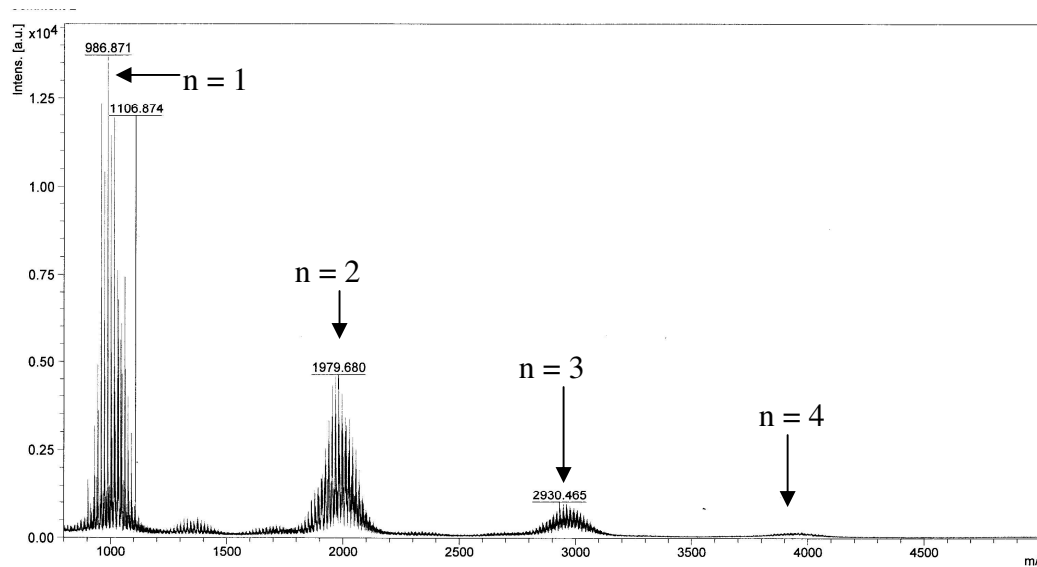


Figure 2.39 MALDI-TOF-MS spectrum of (2.26) by using DHB as the matrix in the analysis

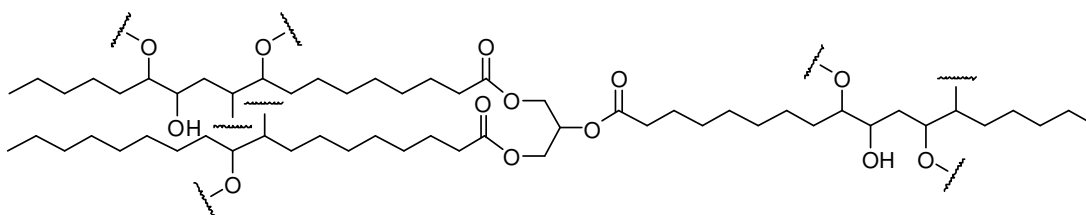


Figure 2.40 Repeating unit in (2.26)

## 2.14 RING OPENING OF EUPHORBIA OIL IN SOLVENT

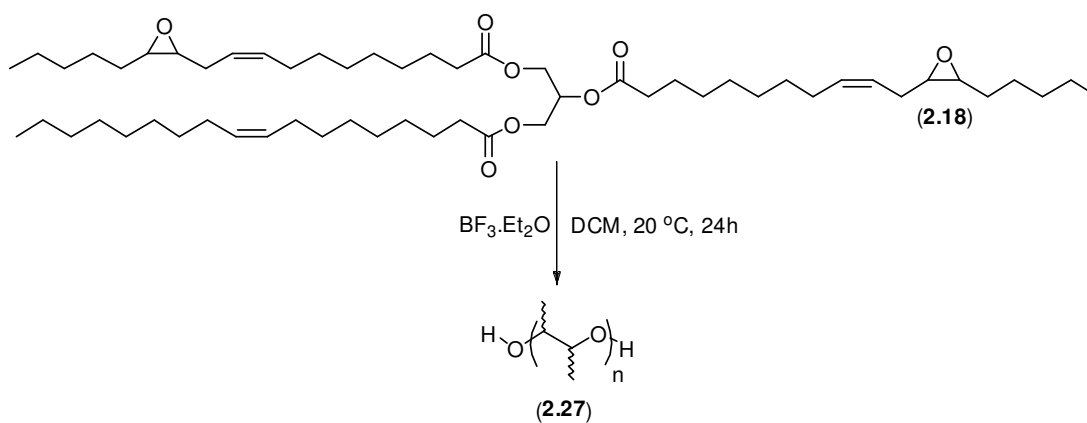


Figure 2.41 Ring opening of (2.18) in solvent with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Finally, the ring opening of the epoxide from euphorbia oil (**2.18**) was examined. This was conducted in similar manner to (**2.6**) (Figure 2.41).

Table 2.15 Properties of products from ring opened (**2.18**)

Entry	Concentration ( $\times 10^{-4}$ mol/ml)	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
				$M_w$ (Da)	$M_n$ (Da)	PDI
1	10.9	0.035	Gelled	-	-	-
2	5.5	0.035	83	26700	8600	3.10
3	3.6	0.035	78	13800	6500	2.14

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

GPC analysis shows that the (**2.27**) has an average molecular weight of 8600 Da, which corresponds to pentamer of (**2.18**) linked by an ether functionality. MALDI-TOF-MS analysis shows that the (**2.27**) has trimer of (**2.18**) linked by ether functionality as shown in Figure 2.42 and with a repeating unit of 913 Da represented by Figure 2.43.

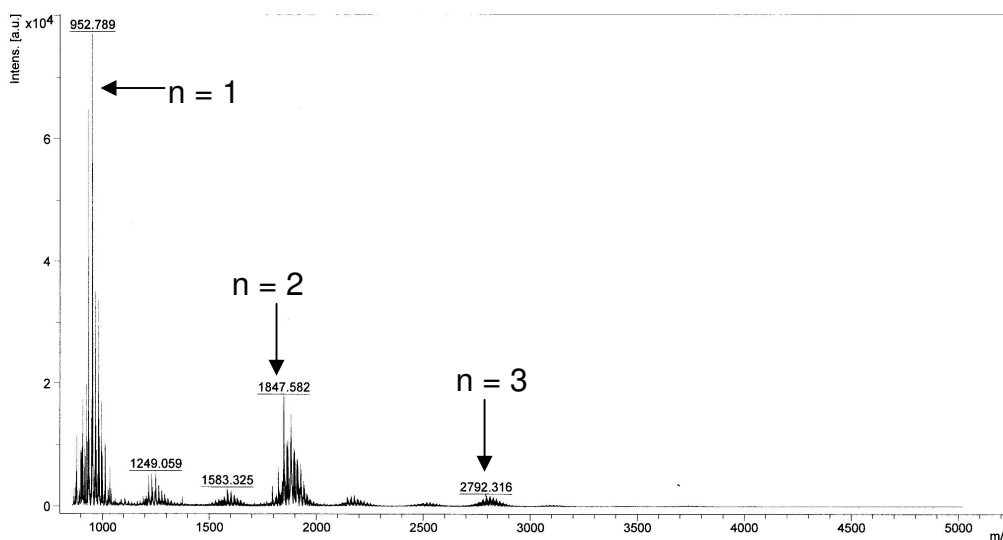


Figure 2.42 MALDI-TOF-MS spectrum of (**2.27**) by using DHB as the matrix in the analysis

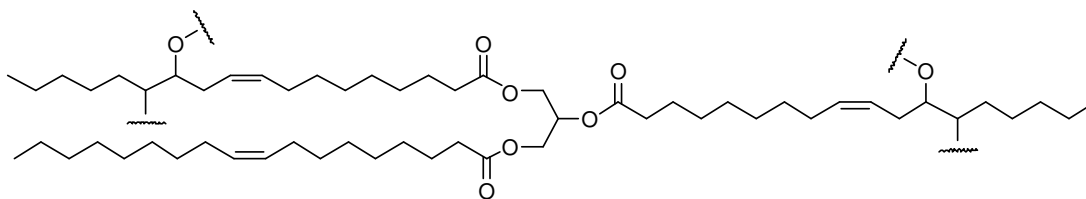
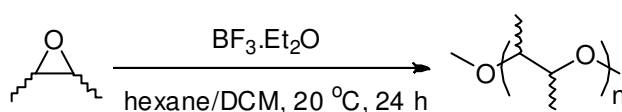


Figure 2.43 Repeating unit in (2.27)

## 2.15 SUMMARY OF RING OPENING OF EPOXIDIZED OILS IN SOLVENT



The following Table 2.16 shows the properties of oligomeric polyols from methyl oleate (2.3) and the 5 types of epoxidized plant oils (2.16, 2.17, 2.13, 2.6 and 2.18) (Figure 2.44). These polyols were produced through the optimum reaction conditions (yield) found for each type of oils. The reaction products were analyzed by  $^1\text{H}$  NMR and GPC.

Table 2.16 Properties of oligomeric polyols from ring opened epoxidized oils

EO	[C]	Mol eq.	Yield (%)	GPC			OHV	AV
				$M_w$ (Da)	$M_n$ (Da)	PDI		
(2.3)	16.0	0.10	85	2100	1900	1.10	51	12
(2.16)	7.1	0.10	87	8400	7300	1.15	30	3
(2.17)	1.9	0.035	87	47000	15500	3.03	38	1
(2.13)	1.1	0.025	90	150000	10000	15.0	48	4
(2.6)	1.1	0.025	90	223000	12600	17.7	88	4
(2.18)	5.5	0.035	83	26700	8600	3.10	36	1

EO = epoxidized oil, [C] = monomer concentration ( $\times 10^{-4}$  mol/ml), Mol eq. = mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , GPC = gel permeation chromatography,  $M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index, OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g)

When the oligomeric polyols from each type of plant oils were compared, epoxidized oils (**2.3**) and (**2.16**) that have one epoxy group per molecule will not form cross-linked polymer even when catalyzed by 0.1 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and both (**2.3**) and (**2.16**) gave good yield of oligomeric polyols (85%, 87%). While for epoxidized oils with multiple epoxide groups per molecule (**2.17**, **2.13**, **2.6** and **2.18**) the amount of catalyst must be less than 0.04 mol equivalents of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  to avoid formation of cross-linked products. Molecules with more epoxides per molecule lead to larger molecular weights, hydroxyl values and PDI's as expected.

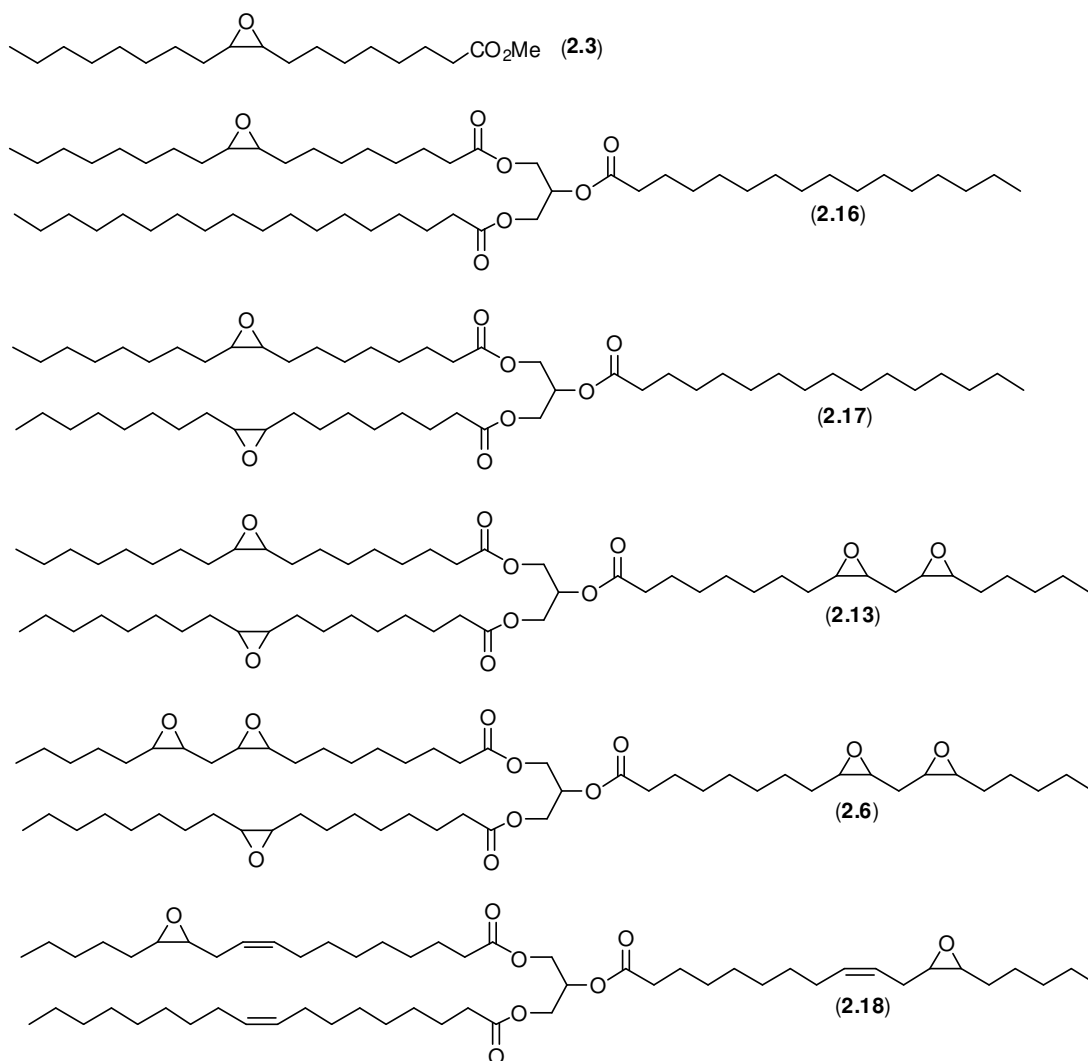


Figure 2.44 Epoxidized plant oils



Both **(2.17)** and **(2.18)** have 2 epoxide groups per molecule and would be expected to behave similarly, but **(2.18)** also has 3 alkenes while **(2.17)** has none. Referring to Table 2.16, we can produce oligomeric polyol without gelling from **(2.18)** using higher monomer concentration ( $5.5 \times 10^{-4}$  mol/ml) as compared to **(2.17)** ( $1.9 \times 10^{-4}$  mol/ml) but with lower  $M_n$  and yield. This indicates that the unsaturation in **(2.18)** helps to prevent cross-linking during the oligomerization reaction which is itself slower. Presumably the extra ‘kink’ on the fatty acid hydrocarbon chain of **(2.18)** is responsible for these properties.

The epoxidized oils **(2.13)** and **(2.6)** have 4 and 5 epoxide groups per molecule respectively, which are higher than the other epoxidized plant oils in this study. This high epoxide content led to higher cross-linking during the oligomerization reaction as shown by the significantly higher  $M_w$  value and hence the higher PDI value of the **(2.25)** and **(2.26)**. The higher epoxide functionality also contributed to slightly higher yield of the oligomeric polyols as well as high hydroxyl values.

Referring to Table 2.16, the hydroxyl value of the oligomeric polyols ranges from 30 to 50 mg KOH/g sample, depending on the starting material. In general, a plant oil with a higher amount of epoxide functionality will produce a higher hydroxyl value because the hydroxyl functionality was produced from the epoxide group through epoxide ring opening reactions. It is noteworthy that the low acid values indicate little hydrolysis (1-4 mg KOH/g sample) however oligomeric polyol **(2.22)** has higher acid value due to the relative ease of hydrolysis of the methyl ester group.

In summary, oligomeric polyols can be produced from various epoxidized plant oils through epoxide ring opening oligomerization catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The properties of the oligomeric polyols depend on the degree of unsaturation of the plant oils as well as the reaction conditions (monomer concentration, catalyst amount, reaction temperature and reaction time).

These oligomeric polyols can theoretically be used to make polyurethane (PU) products as they have hydroxyl groups that can react with diisocyanates. In the later sections, we will compare the properties of PU products made from these oligomeric polyols with PU products made from other plant oils based polyols (ring opening of epoxidized plant oils with polyhydric alcohols and water).

## 2.16 RING OPENING OF EPOXIDIZED OILS WITH POLYHYDRIC ALCOHOLS

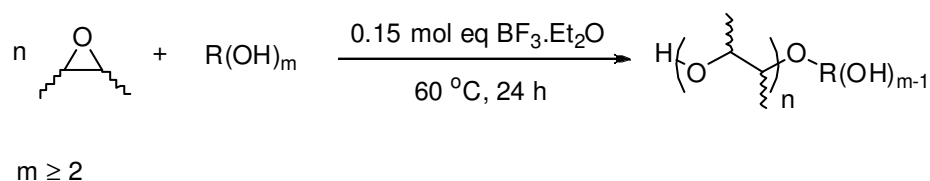


Figure 2.45 Epoxide ring opening with polyhydric alcohol

This study was conducted to investigate the epoxide ring opening oligomerization catalyzed by the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in the presence of a polyhydric alcohol as chain transfer agents (Figure 2.45). The aim for this study is to produce oligomeric polyols that have higher hydroxyl values (from the initiator) compared to oligomeric polyols

produced from epoxidized plant oils through epoxide ring opening in solvent as discussed in Section 2.15 (page 93)

The epoxide ring opening with polyhydric alcohol reaction was conducted without solvent. However, the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was first mixed with the polyhydric alcohol before being added to the epoxidized plant oil. In a way, the polyhydric alcohol acts as solvent for the reaction system as well as the nucleophile for the epoxide ring opening. The epoxidized plant oils (**2.3**, **2.16**, **2.17**, **2.13** and **2.6**) were ring opened with polyhydric alcohols (Figure 2.46) such as ethylene glycol (**2.30**), glycerol (**2.31**), dihydroxy methyl stearate (**2.32**) and glucose (**2.33**). The aim of this section of the work is to incorporate as much renewable content as possible in to the polyol, hence the choice of polyhydric alcohols (**2.31**, **2.32** and **2.33**). Polyhydric alcohol (**2.32**) was prepared from (**2.8**) through epoxidation followed by epoxide ring opening with water. The following Table 2.17 shows the oligomeric content of products from this study as analyzed by GPC.

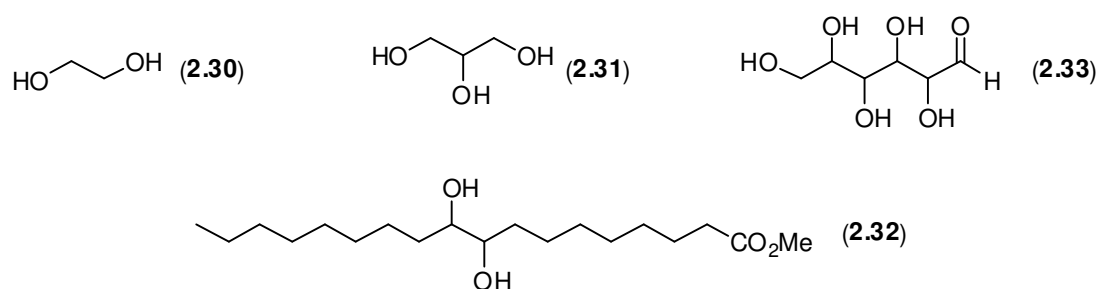


Figure 2.46 Polyhydric alcohols used in epoxide ring opening reaction

Table 2.17 Oligomeric content of ring opened epoxidized oils by polyhydric alcohols.

Epoxidized oil	Oligomeric Content (%)				
	Control	Polyhydric alcohol			
		( <b>2.30</b> )	( <b>2.31</b> )	( <b>2.32</b> )	( <b>2.33</b> )
( <b>2.3</b> )	76	60	77	75	-
( <b>2.16</b> )	56	45	54	34	5
( <b>2.17</b> )	Gelled	70	Gelled	72	14
( <b>2.13</b> )	Gelled	63	Gelled	65	32
( <b>2.6</b> )	Gelled	Gelled	Gelled	80	32

Control reactions were epoxide ring opening reactions conducted without solvent or polyhydric alcohol catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The results of these control reactions were discussed in Section 2.5 (page 71). When the epoxidized plant oils were ring opened with (**2.30**), all the epoxidized oil were converted to liquid oligomeric polyols except for (**2.6**) (Figure 2.47), which gave a cross-linked product (due to its high epoxide value). The (**2.30**) acts as a chain transfer agent and should give rise to lower molecular weight oligomers.

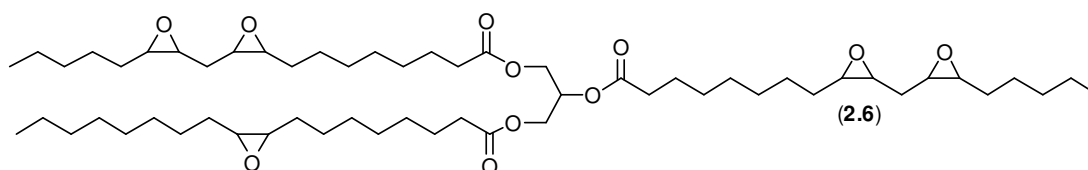


Figure 2.47 Epoxidized soybean oil (**2.6**)

An example of of an oligomeric polyol (**2.34**) produced from (**2.3**) ring opened with (**2.30**) is shown in Figure 2.48. The sodium adduct of this compound was detected by using high resolution mass spectrometry (HRMS) at 709 Da (Figure 2.49).

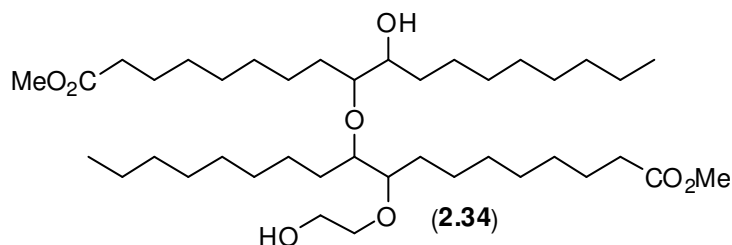


Figure 2.48 Oligomeric polyol (**2.34**)

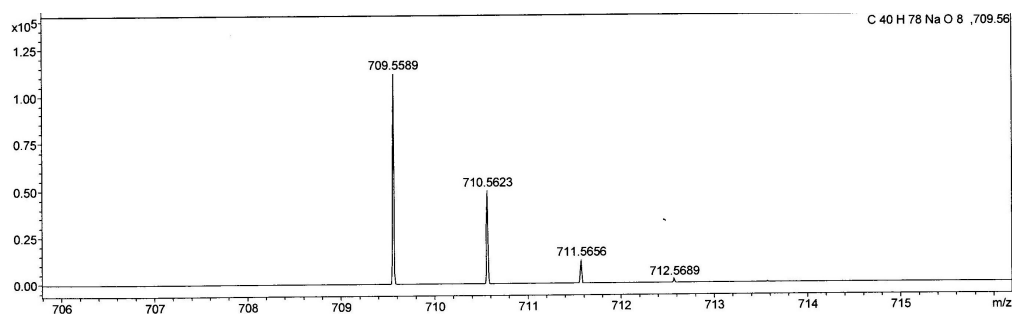


Figure 2.49 High resolution mass spectrum of (**2.34**) in methanol

$^1\text{H}$  NMR analysis on (**2.34**) show peaks at 4.17-4.21 ppm and 3.77-3.82 ppm that correspond to the (**2.30**) moiety linked to (**2.3**) through an ether linkage as shown in Figure 2.48. Another example is the (**2.17**) ring opened with (**2.30**) which yielded oligomeric polyols (**2.35**) that have a repeating unit of 953 Da (Figure 2.50) as shown in MALDI-TOF-MS analysis of the product (Figure 2.51).

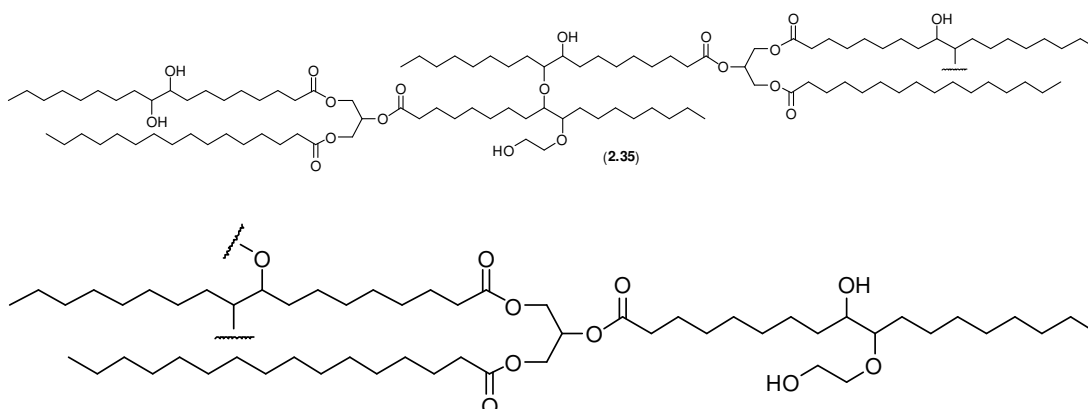


Figure 2.50 Repeating unit of oligomeric polyols (2.35)

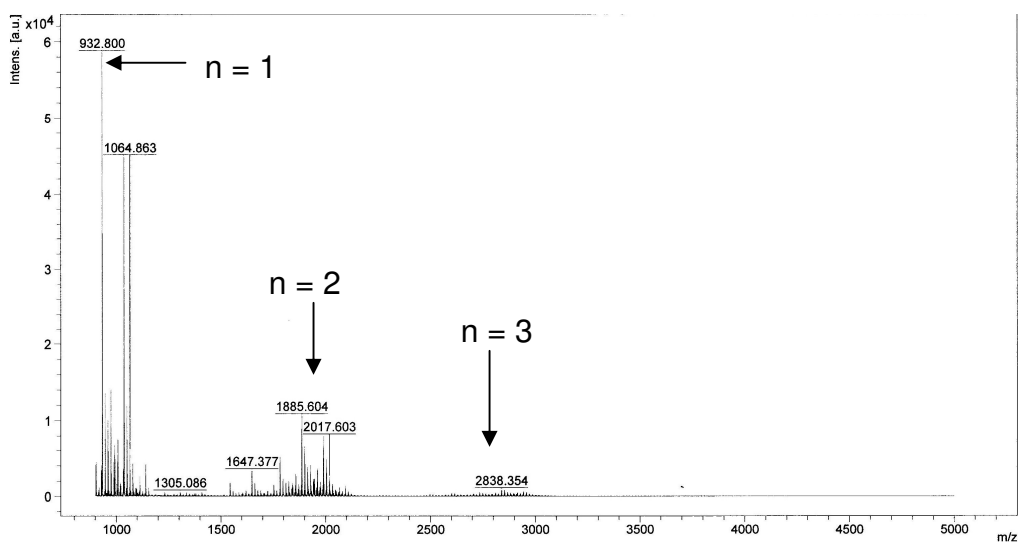


Figure 2.51 MALDI-TOF-MS spectrum of (2.35) by using DHB as the matrix in analysis

Referring to Table 2.17, when (2.31) was used as the polyhydric alcohol in the epoxide ring opening reaction, the results were similar to that of control reactions. This indicates that (2.31) promotes oligomerization and cross-linking between epoxidized plant oils. Therefore, only (2.3) and (2.16) gave oligomeric polyols, while (2.17), (2.13) and (2.6) yielded cross-linked polymers.

The epoxide ring opening of **(2.3)** with **(2.31)** yielded about 75% of oligomeric polyols **(2.36)** that can be represented by Figure 2.52 and was detected by HRMS as a sodium adduct at 1051 Da (Figure 2.53).

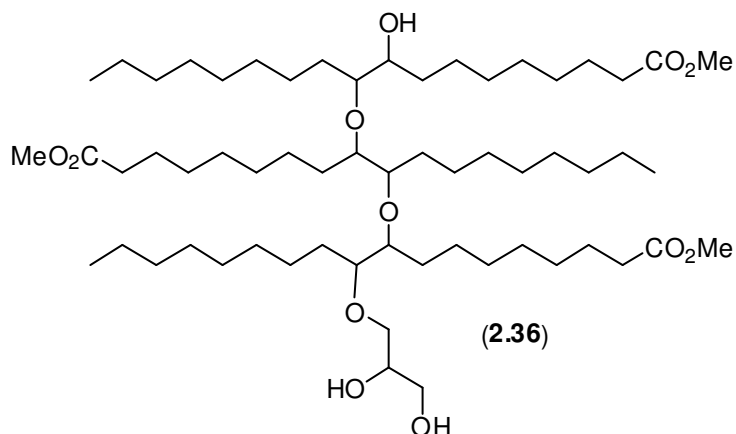


Figure 2.52 Oligomeric polyols **(2.36)**

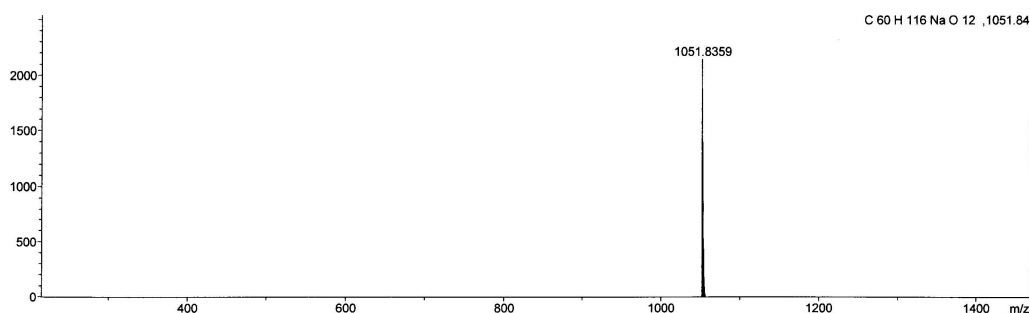


Figure 2.53 High resolution mass spectrum of **(2.36)** in methanol

The other polyhydric alcohol that promotes oligomerization was **(2.32)**. The epoxide ring opening reaction with **(2.32)** yielded 30% to 80% oligomeric polyols depending on the starting materials (as analyzed by GPC). For example, epoxide ring opening of **(2.3)** with **(2.32)** yielded 75% oligomeric polyols **(2.37)** that can be represented by Figure 2.54, and was detected as sodium adduct at 665 Da by HRMS.

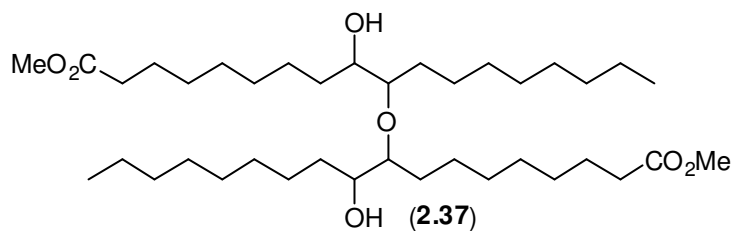
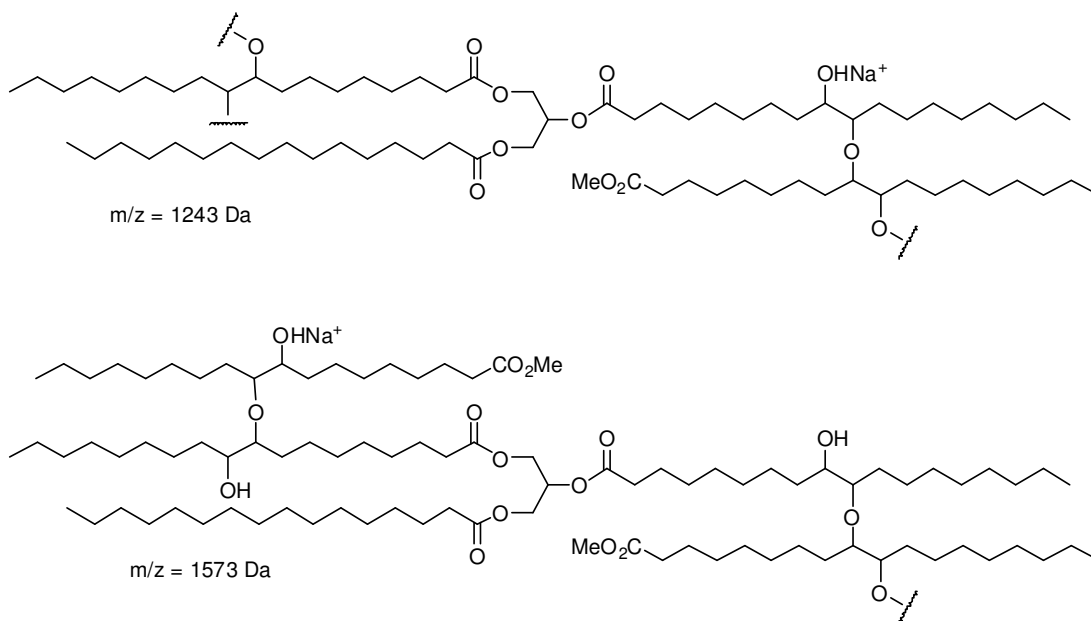


Figure 2.54 Oligomeric polyols of (2.37)

Meanwhile, the epoxide ring opening of (2.17) with (2.32) yielded oligomeric polyols (2.38) that have both the (2.17) and (2.32) as the repeating unit. These mixtures of oligomeric polyols are best illustrated in Figure 2.55; MALDI-TOF-MS analysis indicated sodium adducts at 1243 Da, 1573 Da and 2795 Da respectively (Figure 2.56).





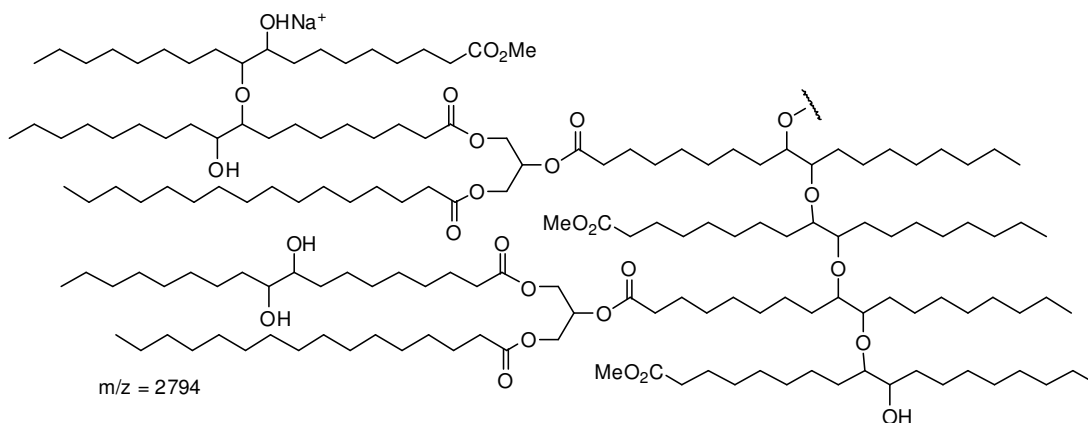


Figure 2.55 Oligomeric polyols (**2.38**)

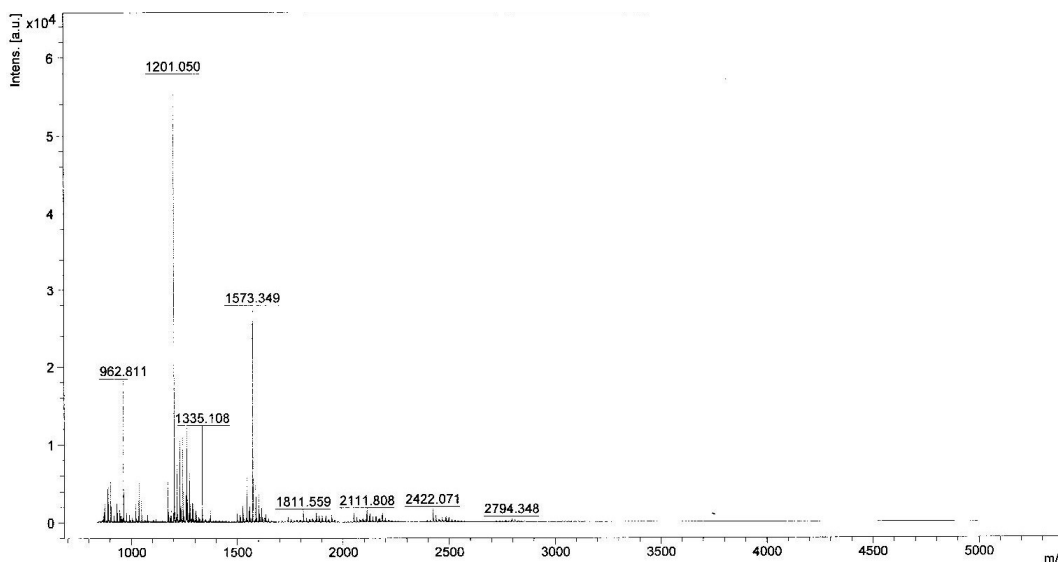


Figure 2.56 MALDI-TOF-MS spectrum of (**2.38**) by using DHB as the matrix in the analysis

Epoxide ring opening reactions with (**2.33**) only produced low amounts of oligomeric compounds (5 – 32%), this may be due to the hydrophilic nature of glucose that did not mix well with hydrophobic epoxidized plant oil or its large number of hydroxyl groups. The following Table 2.18 shows the extent of ring opening oligomerization reaction with polyhydric alcohols in terms of average molecular weight ( $M_n$ ).

Table 2.18 Molecular weight of oligomeric polyols produced from epoxide ring opening with polyhydric alcohol

Epoxidized oil	Average Molecular Weight ( $M_n$ ) (Da)				
	Control	Polyhydric alcohol			
		( <b>2.30</b> )	( <b>2.31</b> )	( <b>2.32</b> )	( <b>2.33</b> )
( <b>2.3</b> )	1700	1400	1800	1700	-
( <b>2.16</b> )	6100	3700	6600	4100	3200
( <b>2.17</b> )	Gelled	9600	Gelled	3100	3300
( <b>2.13</b> )	Gelled	9900	Gelled	2200	3700
( <b>2.6</b> )	Gelled	Gelled	Gelled	1800	4300

$M_n$  = number average molecular weight (Da)

Oligomeric polyols produced from reaction between epoxidized plant oils with multiple epoxy groups (**2.13**) and (**2.17**) and ethylene glycol (**2.30**) shows the highest molecular weight (9600-9900 Da) as compared to epoxidised plant oils with one epoxy group (**2.3**) and (**2.16**). When (**2.3**) and (**2.16**) were ring opened with (**2.33**), the resultant oligomeric polyols have higher molecular weight (1800-6600 Da) as compared to oligomeric polyols produced from the same starting material with other polyhydric alcohols.

In fact, plant oils with multiple epoxide groups (**2.17**, **2.13** and **2.6**) produced cross-linked polymer when reacted with glycerol. Oligomeric products produced from reactions using (**2.32**) and (**2.33**) have relatively low molecular weight as compared to other polyhydric alcohols (**2.30** and **2.31**) may be due to the less reactive secondary alcohol of (**2.32**) and (**2.33**).

The following Table 2.19 shows the hydroxyl values of the oligomeric polyols. The hydroxyl values were higher than the control, and range from 55 to 134 mg KOH/g sample depending on starting material and polyhydric alcohols. This range of hydroxyl values is suitable for the making semi-rigid PU products<sup>34</sup> and is higher than those obtained from the ring opening WITHOUT alcohol initiators prepared in section 2.15. Hence, by using a combination of ring-opening with or without polyhydroxyl initiators it is possible to prepare a palette of hydroxylated materials for a range of PU materials.

Table 2.19 Hydroxyl values of oligomeric polyols produced from epoxidized plant oils ring opened with polyhydric alcohols

Epoxidized oil	Hydroxyl Value (mg KOH/ g sample)			
	Control	Polyhydric alcohol		
		(2.30)	(2.31)	(2.32)
(2.3)	54	110	148	75
(2.16)	39	55	77	69
(2.17)	Gelled	94	Gelled	85
(2.13)	Gelled	134	Gelled	96
(2.6)	Gelled	Gelled	Gelled	118

## 2.17 RING OPENING OF EPOXIDIZED OILS WITH WATER

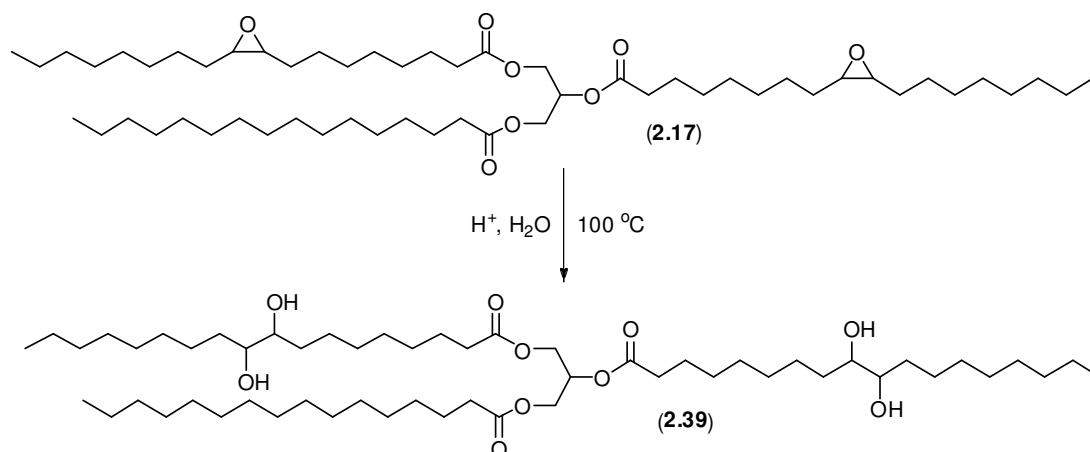


Figure 2.57 Epoxidized plant oil ring opening with water

Finally, the ring-opening of epoxidized oils with water under acid catalysis was explored. The aim of this part of the work was to prepare plant oil based polyols without ring-opening oligomerization (Figure 2.57). The *monomeric* hydroxylated plant oil polyols would act as the reference point for comparison of the materials properties of PU products made from oligomeric polyols prepared earlier in section 2.15 and 2.16.

For this study, (2.17) and (2.6) were selected as the starting materials because they are the most studied plant oils.<sup>10, 89</sup> They were ring opened with water at  $100\text{ }^\circ\text{C}$  in the presence of an acid catalyst to produce hydroxylated palm oil polyol (2.39) and hydroxylated soybean oil polyol (2.40) (Figure 2.58). The reaction products were analyzed by GPC,  $^1\text{H}$  NMR and the properties of these hydroxylated plant oil polyols were tabulated in Table 2.19

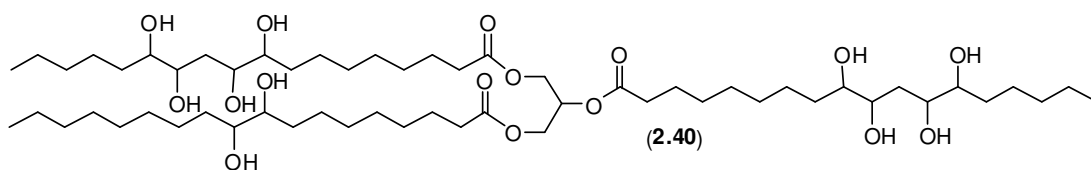


Figure 2.58 Hydroxylated soybean oil polyol **(2.40)**

Table 2.19 Properties of hydroxylated plant oil polyols

Polyol	Yield (%)	Oligomers content (%)	GPC			OHV	AV
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI		
<b>(2.39)</b>	95	30	3800	3400	1.12	70	12
<b>(2.40)</b>	90	60	14700	8300	1.77	112	18

GPC = gel permeation chromatography, M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index, OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g)

Referring to Table 2.19, the epoxide ring opening reaction with water catalyzed by *para*-toluene sulfonic acid (*p*-TSA) gave significant amount of oligomers (30-60%). The **(2.6)** gave a higher amount of oligomers due to the higher epoxide functionality of **(2.6)** as compared to **(2.17)** and thus more likely to form oligomers.

In addition, the higher epoxide functionality of **(2.6)** also gave higher hydroxyl values as compared to **(2.17)**. However, due to the high amount of oligomers found in **(2.40)**, it was deemed not suitable as reference point for our study in order to compare the properties of PU made from plant oil based *monomeric* polyols and *oligomeric* polyols. Therefore no further analysis was done on **(2.40)**.

The epoxide ring opening with water catalyzed by *p*-TSA, also causes hydrolysis of the triglyceride as a side reaction. Based on the hydroxyl value and molecular weight alone, both hydroxylated polyols (**2.39** and **2.40**) are suitable for making semi-rigid to rigid PU products.

## CHAPTER 3 – SYNTHESIS OF POLYURETHANES

### 3.1 - POLYURETHANES MADE FROM PLANT OIL BASED POLYOLS

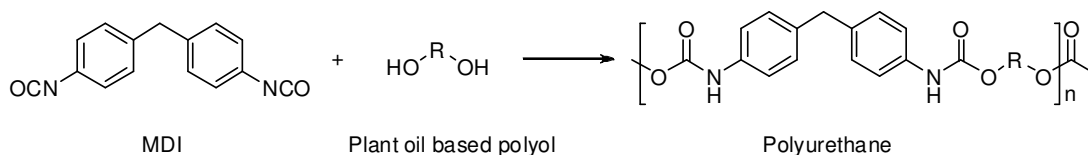


Figure 3.1 Synthesis of PU from MDI and plant oil based polyol

The prepared plant oil based *oligomeric polyols* (OP) as well as the *monomeric hydroxylated* plant oil polyols (HP) were used as starting materials for making PU samples. These polyols were reacted with 4,4'-diphenylmethane diisocyanate (MDI) (Figure 3.1) and yielded quantitative amounts of PU samples. The ratio between the isocyanate group (NCO) and the hydroxyl group (OH) was kept at 1.05 to 1 (NCO/OH ratio = 1.05) in order to ensure that all the hydroxyl groups of the plant oil based polyols (POP) were fully reacted and the PU samples were fully cured when the excess isocyanate group reacted with moisture from the air.

The PU synthesis was started with the six OP (2.22, 2.23, 2.24, 2.25, 2.26 and 2.27) prepared in Chapter 2 and they were reacted with MDI according to ratio describe above. The PU's (3.1 and 3.2) made from (2.22) and (2.23) were pastes/viscous liquids at room temperature, while for the other OP, the PU's made from them were solids at room temperature. Thus the PU's (3.3, 3.4, 3.5 and 3.6) made from (2.24), (2.25), (2.26) and (2.27) respectively were cross-linked polymers at room temperature, indicating higher than 2 hydroxyl groups per molecule of macromonomer to enable the formation of network/cross-linked polymers.

#### Oligomeric Polyols (*OP*)

- (2.22) – Oligomeric polyol based on epoxidized methyl oleate (2.3)
- (2.23) – Oligomeric polyol based on epoxidized cocoa butter (2.16)
- (2.24) – Oligomeric polyol based on epoxidized palm oil (2.17)
- (2.25) – Oligomeric polyol based on epoxidized rapeseed oil (2.13)
- (2.26) – Oligomeric polyol based on epoxidized soybean oil (2.6)
- (2.27) – Oligomeric polyol based on euphorbia oil (2.18)

#### Polyurethane samples (*PU*)

- (3.1) – PU based on oligomeric polyol (2.22)
- (3.2) – PU based on oligomeric polyol (2.23)
- (3.3) – PU based on oligomeric polyol (2.24)
- (3.4) – PU based on oligomeric polyol (2.25)
- (3.5) – PU based on oligomeric polyol (2.26)
- (3.6) – PU based on oligomeric polyol (2.27)
- (3.7) – PU based on hydroxylated palm oil polyol (2.39)

Tensile tests were carried out on these solid PU's in order to give a better picture about their strength. Figure 3.2 shows the stress-strain curves of PU's made from each type of *OP*. In addition, we have also included *HP* based PU (3.7) made from (2.39) in Figure 3.2 for comparison purposes. The PU made from (2.40) was not included in Figure 3.2 because the PU made from it was too brittle to make a tensile test sample. The properties of these PU will be discussed in following pages.



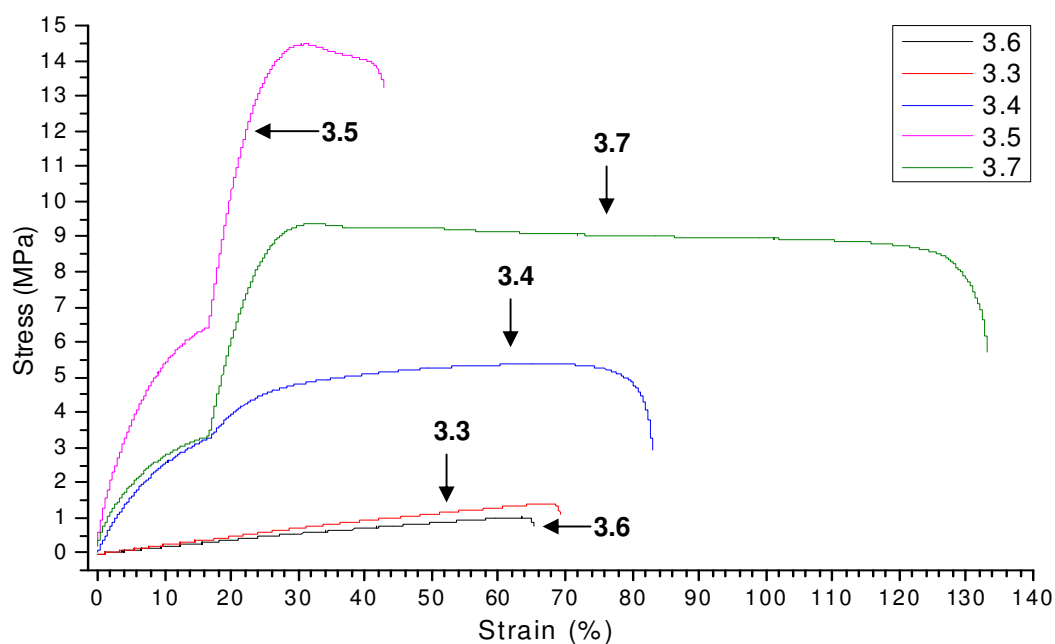


Figure 3.2 Stress-strain curves of PU samples made from *OP* and *HP* based polyols according to method EN ISO 529-4: 1997(CEN1997a)

Furthermore, swelling tests was conducted on each of the PU samples in order to determine the cross-link density by using the Flory-Rehner equation.<sup>95</sup> The following Table 3.1 shows the properties of the PU samples made from *OP* and *HP* based polyols.

Table 3.1 Properties of the PU samples made from *OP* and *HP* based polyols

PU	Tensile strength (MPa)	Elongation at break (%)	Cross-link density $\times 10^{-4}$ (mol/cm <sup>3</sup> )
(3.6)	0.8	66	1.9
(3.3)	1.0	70	2.0
(3.4)	5.0	80	4.5
(3.5)	14.0	40	8.9
(3.7)	9.0	130	6.5

Referring to Figure 3.2 and Table 3.1, the PU samples (3.6) and (3.3) have low tensile strength ( $\sim 1$  MPa) and elongation at break ( $\sim 70\%$ ). This was due to the relatively low hydroxyl value (36 and 38 mg KOH/g sample) of *OP* (2.27) and (2.24) compared to (2.25) and (2.26). The lower hydroxyl values yielded PU samples with lower cross-linking density ( $1.9$  and  $2.0 \times 10^{-4}$  mol/cm<sup>3</sup> respectively) which therefore exhibited lower tensile strength and elongation. In comparison, PU sample (3.4) has a higher tensile strength (5 MPa) and elongation (80%) because the (2.25) has higher hydroxyl value (48 mg KOH/g sample) as well as cross-link density ( $4.5 \times 10^{-4}$  mol/cm<sup>3</sup>) than both (2.27) and (2.24).

The PU sample (3.5) exhibited even higher tensile strength (14.5 MPa) because of the high cross-linking density ( $8.9 \times 10^{-4}$  mol/cm<sup>3</sup>) in the PU sample that originated from the high hydroxyl value (88 mg KOH/g sample) of (2.26). However, the cross-linking density of (3.5) was high enough to restrict the movement of polymer chain that it becomes so rigid until elongation of the PU sample was limited and it snapped with increasing tensile strength, resulted in lower elongation (40%) as shown in Figure 3.2.

The PU (3.7) made from (2.39) exhibited tensile strength in between (3.5) and (3.4) because (2.39) has hydroxyl value (70 mg KOH/g sample) and cross-link density ( $6.5 \times 10^{-4}$  mol/cm<sup>3</sup>) in between the two *OP*. However, (3.7) exhibited higher elongation than (3.5) and (3.4) maybe because of the plasticizing effect from saturated fatty acid in the (2.39) that enable elongation of the PU sample.

### 3.2 POLYURETHANES MADE FROM PLANT OIL BASED POLYOLS AND 1,4-BUTANEDIOL

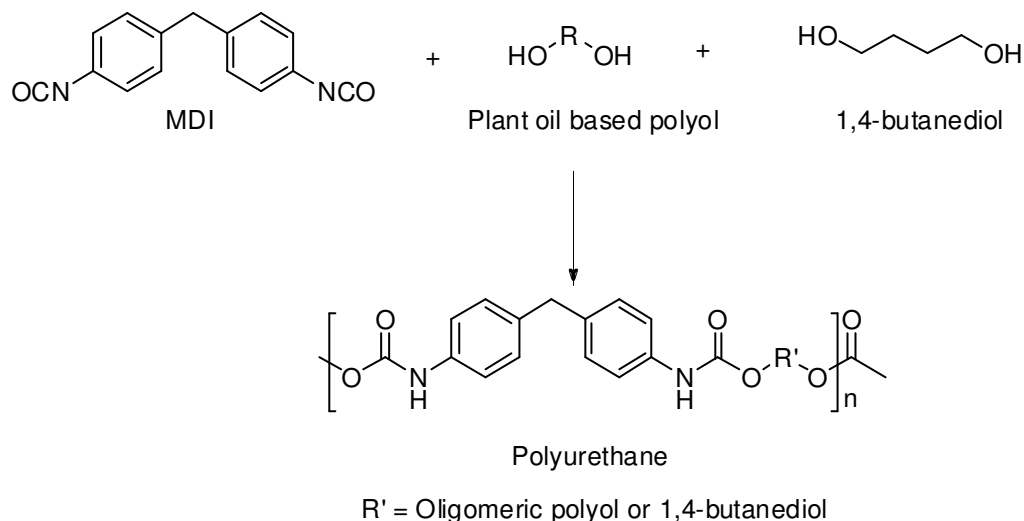


Figure 3.3 PU made from plant oil based polyol and 1,4-butanediol

In the production of elastomeric polyurethane, it is very common to include chain extenders in the PU formulation in order to improve the properties of the PU products. The chain extender acts as the hard segment domain of PU that strengthens the PU through hydrogen bonding among urethane bonds.<sup>8</sup> In order to strengthen the PU made from *OP* prepared in section 2.15, a chain extender such as 1,4-butanediol (**3.8**) was mixed with the *OP* macromonomer in the PU formulation (Figure 3.3). For this study (**2.24**) was chosen as the *OP* to investigate since (**3.3**) exhibited low tensile strength in the study conducted in section 3.1 (page 109)

The (**2.24**) was mixed with varying amount of (**3.8**) to yield PU samples with hard segments ranging from 10% to 50%. Meanwhile, the NCO/OH ratio was kept at 1.05/1, similar to previous study in section 3.1. The PU samples made from (**2.24**) and (**3.8**) were subjected to a quick test in which the PU samples were pulled at both

end with the bare hands to evaluate the strength of the samples. The following Table 3.2 shows the strength and physical properties of the prepared PU samples of this study.

Table 3.2 Physical properties and strength of the PU samples

Hard segment (%)	Physical properties	Pull apart by hand?
10	Soft elastic solid	yes
20	Soft elastic solid	yes
30	Hard brittle solid	yes
40	Hard brittle solid	yes
50	Hard brittle solid	yes

Referring to Table 2.21, the physical properties of the PU samples changes from soft elastic to hard brittle as the hard segment of the PU sample increases from 10% to 50%. This shows that the increasing amount of **(3.8)** makes the PU sample more hard and brittle. However, all the PU samples made with **(3.3)** and **(3.8)** have failed the quick test, which indicates that the **(3.8)** is not strengthening the PU samples even at high percentages. It made the PU brittle at high percentages because the urethane linkages formed from reaction with the diisocyanate were too close to each other. This is because **(3.8)** is a small molecule and doesn't strengthen PU as well as higher molecular weight polyols such as polyethylene glycol.

### 3.3 POLYURETHANES MADE FROM OLIGOMERIC POLYOLS AND POLYETHYLENE GLYCOL

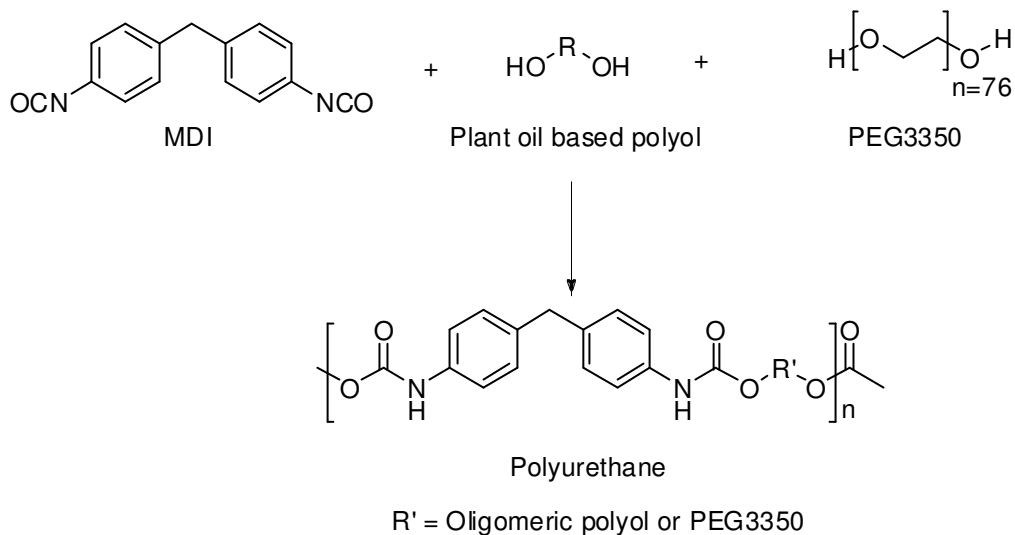


Figure 3.4 PU made from plant oil based polyol and PEG3350

Based on the results from the quick test performed on PU made from (2.24) and (3.8), we decided to mix (2.24) with higher molecular weight diols such as polyethylene glycol 3350 (3.9) (average molecular weight of 3350 Da) and use this polyol mixture as a starting material to react with MDI (Figure 3.4). The (2.24) was mixed varying amount of (3.9) to yield PU samples with hard segment ranging from 30% to 70%. Meanwhile, the NCO/OH ratio was kept at 1.05/1, similar to previous study in section 3.1. The prepared PU samples were subjected to the same quick test. The following Table 3.3 shows the result of this study.

Table 3.3 Physical properties and strength of the PU samples

Hard segment (%)	Physical properties	Pull apart by hand?
30	Soft elastic solid	yes
40	Soft elastic solid	yes
50	Elastic solid	yes
60	Elastic solid	no
70	Hard brittle solid	no

The results in Table 3.3 shows that the PU samples change from soft elastic PU to elastic solid PU and then to hard brittle PU as the hard segment of PEG of the PU increases from 30% to 70%. In addition, the strength of the PU samples increases with the increase in hard segment, in which at 60% hard segment, the PU can now not be pulled apart by a bare hand. At 70% hard segment, the PU sample was found to be brittle and breaks apart easily.

The PU sample with 60% hard segment exhibited acceptable physical properties; therefore tensile test samples were made based on this formulation. The PU sample with 60% hard segment was made from a 1:1 ratio of (2.24) to (3.9) based on hydroxyl value equivalent weight. The same ratio was used for other *OP* (2.25, 2.26 and 2.27) in making PU samples that incorporates (3.9) in order to compare the physical properties of the PU samples from different *OP*. These new materials were labeled as (3.10), (3.11), (3.12) and (3.13) for PU based on (2.24), (2.25), (2.26) and (2.27) respectively. The *HP* (2.39) was also included into the study for comparison purposes (abbreviated as 3.14). In addition, PU made from only (3.9) and MDI was also included as a control (abbreviated as 3.15).

The following Figure 3.5 shows the stress strain curves of PU's made from combination of *OP* and *HP* with (3.9); (3.9) alone; and as a comparison those described earlier in section 3.1 (3.3, 3.4, 3.5, 3.6 and 3.7). Furthermore, the properties of these PU were tabulated in Table 3.4.

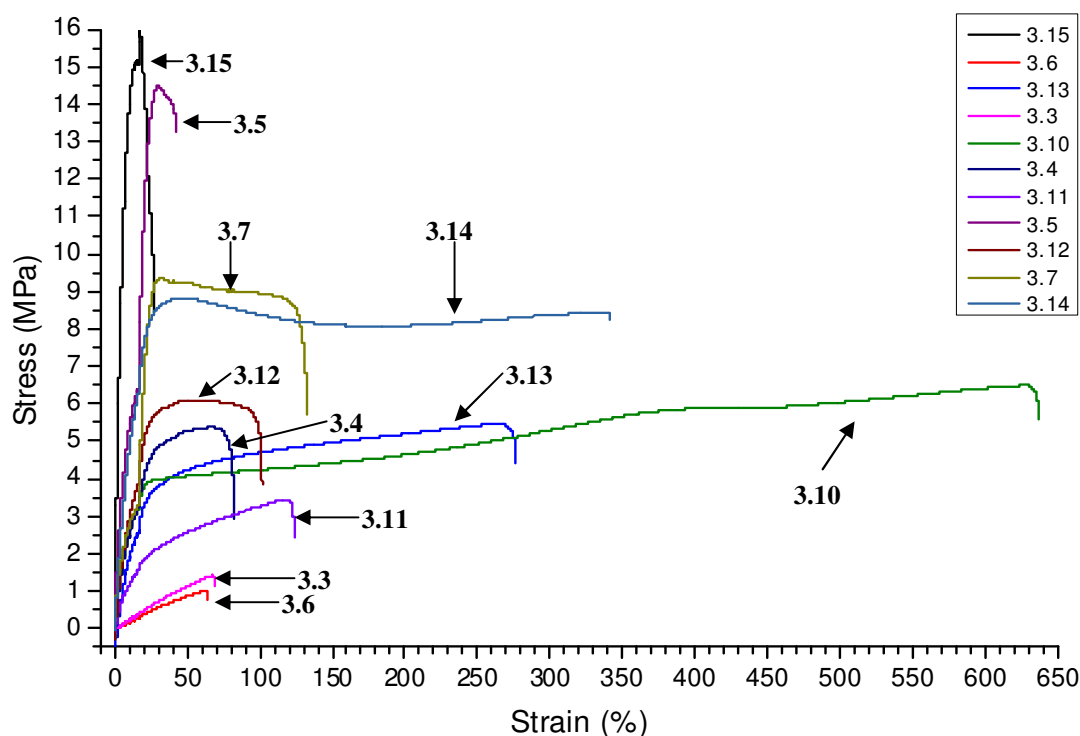


Figure 3.5 Stress strain curve of PU made from *OP*, *HP* and (3.9) according to method EN ISO 529-4: 1997(CEN1997a)

#### Polyurethane samples (PU)

- (3.3) – PU based on oligomeric polyol (2.24); (palm oil based)
- (3.4) – PU based on oligomeric polyol (2.25); (rapeseed oil based)
- (3.5) – PU based on oligomeric polyol (2.26); (soybean oil based)
- (3.6) – PU based on oligomeric polyol (2.27); (euphorbia oil based)
- (3.7) – PU based on hydroxylated palm oil polyol (2.39)
- (3.10) – PU based on oligomeric polyol (2.24) and PEG3350 (3.9)
- (3.11) – PU based on oligomeric polyol (2.25) and PEG3350 (3.9)
- (3.12) – PU based on oligomeric polyol (2.26) and PEG3350 (3.9)
- (3.13) – PU based on oligomeric polyol (2.27) and PEG3350 (3.9)
- (3.14) – PU based on hydroxylated palm oil (2.39) and PEG3350 (3.9)
- (3.15) – PU based on PEG3350 (3.9) and MDI

Table 3.4 Properties of the PU samples made from *OP*, *HP* and **(3.9)**

PU	Tensile strength (MPa)	Elongation at break (%)	Cross-link density $\times 10^{-4}$ (mol/cm <sup>3</sup> )
<b>(3.15)</b>	16.0	20	0.0
<b>(3.6)</b>	0.8	66	1.9
<b>(3.13)</b>	5.5	270	3.5
<b>(3.3)</b>	1.0	70	2.0
<b>(3.10)</b>	6.5	650	3.5
<b>(3.4)</b>	5.0	80	4.5
<b>(3.11)</b>	3.5	120	3.8
<b>(3.5)</b>	14.0	40	8.9
<b>(3.12)</b>	6.0	100	4.3
<b>(3.7)</b>	9.0	130	6.5
<b>(3.14)</b>	8.8	350	5.6

#### PU **(3.15)**

Referring to Figure 3.5 and Table 3.4, the control PU sample **(3.15)** made from only **(3.9)** and MDI shows significantly high tensile strength (16 MPa) but low elongation (20%). The high tensile of **(3.15)** comes from the intermolecular forces between polymer chains of **(3.15)** as the PU can form a semicrystalline structure in which the crystalline **(3.9)** chains can act as a physical cross-link in the polymer matrix.<sup>96</sup> However, the cross-link density of **(3.15)** was near to zero because both the **(3.9)** and MDI are bifunctional linear molecules, which cannot form cross-linking. The **(3.15)** sample completely dissolved in the test solvent (toluene)



#### PU (3.10) and (3.13)

When the *OP* of similar hydroxyl value (2.24 and 2.27) were mixed with (3.9) and reacted with MDI to form PU samples (3.10) and (3.13); the tensile strength (6.5 MPa and 5.5 MPa respectively) of these PU samples was found to be better than PU samples made from only the *OP* (3.3 and 3.6). This higher tensile strength was contributed by higher cross-link density found in the two PU samples ( $3.5 \times 10^{-4}$  mol/cm<sup>3</sup> vs  $\sim 2.0 \times 10^{-4}$  mol/cm<sup>3</sup> respectively).

The most significant improvement on the properties of (3.10) and (3.13) compared to (3.3), (3.6) and (3.15) is the elongation at break. The (3.13) was able to extend 270% its original length, while (3.10) was able to extend 650% its original length before breaking. In comparison, the (3.15), (3.6) and (3.3) were only able to extend 20%, 66% and 70% respectively. Referring to both tensile strength and elongation at break for (3.10) and (3.13), *which point to the synergy from the co-polymerization of petroleum-based polyol (3.9) with plant oil based oligomeric polyols (2.24 and 2.27) to form PU (by reaction with MDI) as the PU formed from this mixture of polyols performed better than the PU made from either individual polyol respectively.*

#### PU (3.11) and (3.12)

For PU samples (3.11) and (3.12), the mixture of (3.9) and *OP* (2.25 and 2.26) have resulted in PU with significantly lower tensile strength (3.11, 3.5 MPa and 3.12, 6.0 MPa) as compared to PU made from *OP* alone (3.4, 5.0 MPa and 3.5, 14 MPa). This is in tandem with the lower cross-link density exhibited by the (3.11) and (3.12). However, the lower tensile strength of the (3.11) and (3.12) was compensated by longer elongation of these PU samples (130% and 100% respectively) as compared

to (3.4) and (3.5). Overall, the mixtures of (3.9) with (2.25) and (2.26) have resulted in PU with poorer properties due to lower cross-link density exhibited by the (3.11) and (3.12).

#### PU (3.14)

For PU samples (3.14), the mixture of (3.9) and *HP* (2.39) has resulted in a PU with a slightly lower tensile strength as compared to PU (3.7) made from (2.39) only. This is in tandem with the lower cross-link density exhibited by the (3.14). However, the lower tensile strength of the (3.14) was compensated by significantly longer elongation (350%), which was double the elongation achieved by (3.7).

### **3.4 POLYURETHANES MADE FROM EPOXIDIZED PALM OIL BASED POLYOLS PREPARED BY DIFFERENT METHODS**

For this part of the study, various types of PU samples based on epoxidized palm oil (2.17) were prepared in order to determine how the different (2.17) based polyols (2.24, 2.38 and 2.39) affect the properties of a PU when incorporating (3.9). The prepared (2.17) based PU's were (3.3), (3.10), (3.7), (3.14) and (3.16).

The properties of the PU samples (3.15), (3.3), (3.10), (3.7), and (3.14) were discussed earlier in Section 3.3. Thus the last material of the set to prepare was (3.16) from the palm oil macromonomer (2.38) prepared by reacting (2.17) with (2.32) as a ring-opening initiator, (see section 2.16, page 97). The (2.38) was reacted with MDI

but the PU produced from the reaction was a viscous paste, which indicated that the PU sample did not have sufficient cross-link density to form a solid PU.

Therefore, in order to make solid PU from (2.38), we mixed the (2.38) with (3.9) and the tensile strength of the PU (3.16) can be seen in Figure 3.6, which is the stress-strain curve of (3.16).

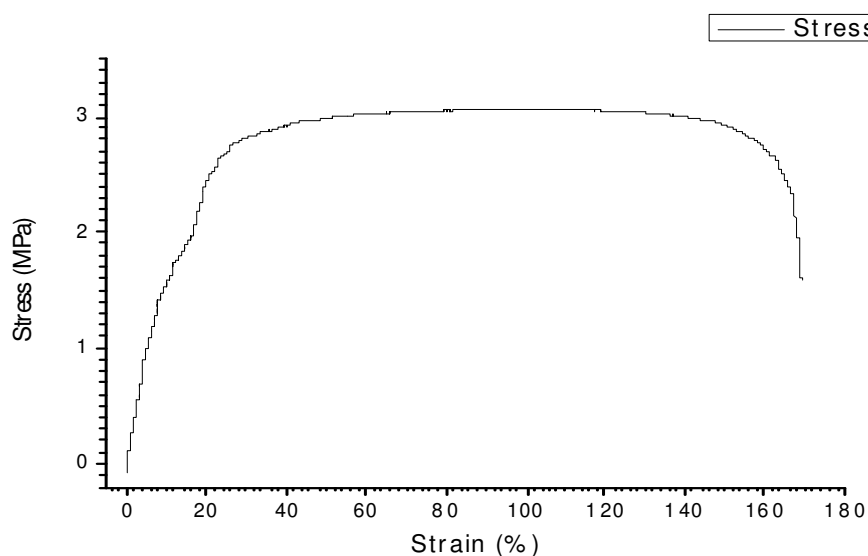


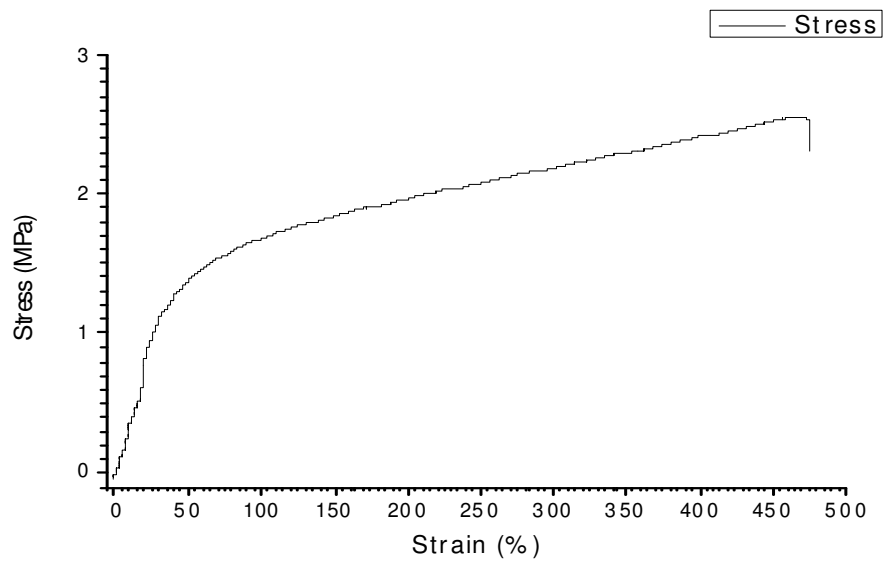
Figure 3.6 Stress strain curve of (3.16) according to method EN ISO 529-4: 1997(CEN1997a)

The (3.16) exhibited about 3 MPa of tensile strength and 170% elongation. In comparison with (3.10), the (3.16) showed inferior properties. In summary, this shows that the (2.38) was inferior to (2.24) (refer to Figure 3.5) in making PU products maybe due to the relatively low molecular weight of (2.38) as compared to (2.24).

### 3.5 POLYURETHANES MADE FROM EPOXIDIZED METHYL OLEATE AND EPOXIDIZED COCOA BUTTER BASED POLYOLS

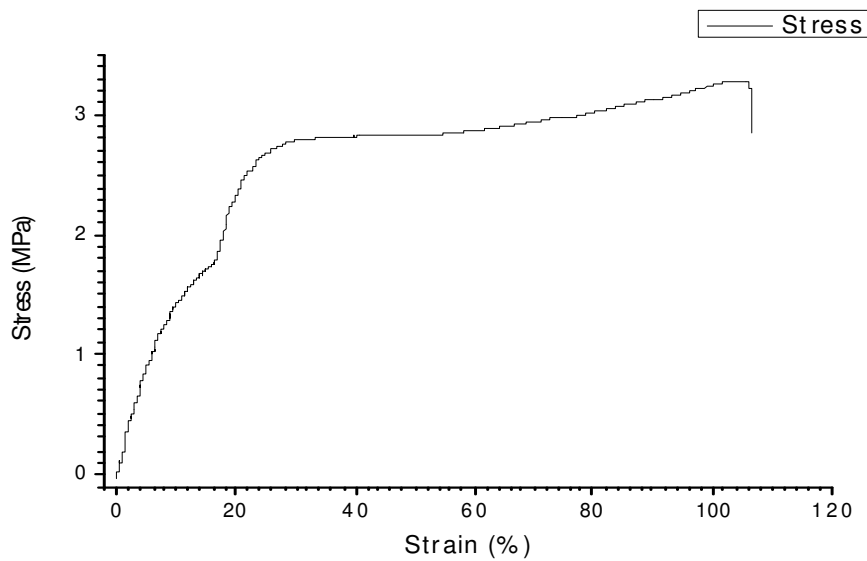
In the previous section the PU's from palm oil, rapeseed oil and soya bean oil were discussed. This section investigates the PU's prepared from the *OP* (2.22) and (2.23). The PU samples made from these two *OP* were viscous pastes at room temperature. Thus, as with (2.38) above, we mixed the (2.22) and (2.23) with (3.9) in order to make a solid PU; however the resultant PU's were still viscous pastes. This suggests that both (2.22) and (2.23) do not have enough cross-linking to form a solid PU due to their low hydroxyl values and mixing them with PEG3350 did not help either for the same reason.

In order to make solid PU from (2.22) and (2.23), glycerol (2.31) was introduced into the PU formulation. The (2.31) was chosen because in order to use more renewable raw material in the PU sample. The hydroxyl group ratio between (3.9): (2.22): (2.31) was 1:1:3 and the NCO/OH ratio was kept at 1.05/1. This combination of polyols was able to produce a solid PU. The prepared PU samples, methyl oleate derivative (3.17) and the cocoa butter derivative (3.18) were subjected to tensile tests to evaluate their mechanical properties. The following Figures 3.7 and 3.8 show the stress-strain curves of (3.17) and (3.18) respectively.



11

Figure 3.7 Stress-strain curve of **(3.17)** according to method EN ISO 529-4: 1997(CEN1997a)



12

Figure 3.8 Stress-strain curve of **(3.18)** according to method EN ISO 529-4: 1997(CEN1997a)

Referring to Figure 2.61, the incorporation of **(2.31)** in the PU formulation has enabled the production of a PU sample **(3.17)** with good elongation at break (470%) from **(2.22)** even though the tensile strength was relatively low. This shows that **(2.22)** itself contributed to the flexibility of the PU sample. For cocoa butter the

analogous PU sample **(3.18)** shows better tensile strength (3.5 MPa) than **(3.17)**; however the elongation at break was only 100%, which shows the **(3.18)** was stiffer than **(3.17)**. In summary, the incorporation of **(2.31)** was necessary in the formulations of PU in order to make solid PU from **(2.22)** and **(2.23)** due to low hydroxyl value of both oligomeric polyols.

### 3.6 SUMMARY

Unsaturated plant oils can be converted to epoxidized plant oils through epoxidation with hydrogen peroxide as the oxidant and tungsten powder as the catalyst. The prepared epoxidized plant oils can be oligomerized to yield *OP* through epoxide ring opening conducted in solvent and catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . This oligomerization reaction was affected by the amount of catalyst, reaction temperature, reaction duration and the concentration of the monomer (epoxidized plant oils). The properties of these *OP* also depended on the degree of unsaturation of the plant oils. Plant oils with low unsaturation (**2.8** and **2.9**) will yield *OP* with lower molecular weight; while plant oils with two or more unsaturation points will produce high molecular weight polyols with higher hydroxyl values and PDI's.

These prepared *OP* were used to make PU samples with MDI. Generally, the PU's based on *OP* made from plant oils with low levels of unsaturation (**2.22** and **2.23**) formed viscous paste PU samples. While, PU's based on *OP* made from plant oils with higher level of unsaturation (**2.24**, **2.25**, **2.26** and **2.27**) formed solid PU samples. The PU based on **(2.26)** had the highest tensile strength but the lowest elongation at

break of all the oils tested. In comparison, PU's based on (2.24), (2.25) and (2.27) have significantly lower tensile strengths but higher elongation at break.

The PU samples based on (2.24) and (2.27) can be strengthened by mixing them with (3.9), which increased the tensile strength and elongation at break significantly. However, when (2.25) and (2.26) were mixed with (3.9), the tensile strength of the PU samples based on them were weaker than those without (3.9). Solid PU samples can be made from *OP* (2.22) and (2.23) by mixing them with (3.9) and (2.31). The (2.31) component contributed to cross-linking that enables a solid PU to be prepared from these oligomeric polyols.

The mechanical properties analysis of PU samples (3.10), (3.13) and (3.14) indicates that these PU samples were suitable for making elastomeric PU where high flexibility (high elongation at break) of the PU is a requirement. On the other hand, PU sample (3.5) was found to have mechanical properties suitable for semi-flexible PU elastomer where high tensile strength with low elongation at break is a common requirement.

## CHAPTER 4 – COPOLYMERIZATION OF EPOXIDIZED PLANT OILS WITH HETEROCYCLES

### 4.0 INTRODUCTION

Polytetrahydrofuran (PTHF) is obtained from tetrahydrofuran (THF) through cationic polymerization (Figure 3.1) catalyzed by strong Lewis acids ( $\text{BF}_3$ ,  $\text{SbF}_5$ )<sup>32</sup> or strong Bronsted acids ( $\text{FSO}_3\text{H}$ ,  $\text{CF}_3\text{SO}_2\text{OSO}_2\text{CF}_3$ ).<sup>32</sup>

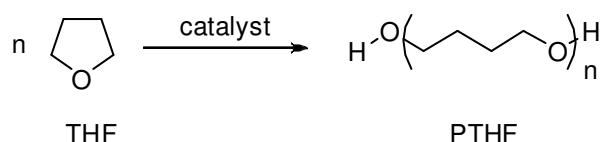


Figure 4.1 Polymerization of tetrahydrofuran

The ring opening polymerization of THF is driven by the ring strain of THF which is around 5.63 kcal/mol. The ring strain of THF is smaller than the ring strain of alkylene oxides (27.28 kcal/mol)<sup>97</sup> but is high enough for ring opening polymerization of THF. The ring strain of THF is mostly contributed by the torsional repulsion forces between hydrogen atoms situated in eclipsed positions (Figure 4.2) and a small contribution from angular tension.<sup>98</sup>

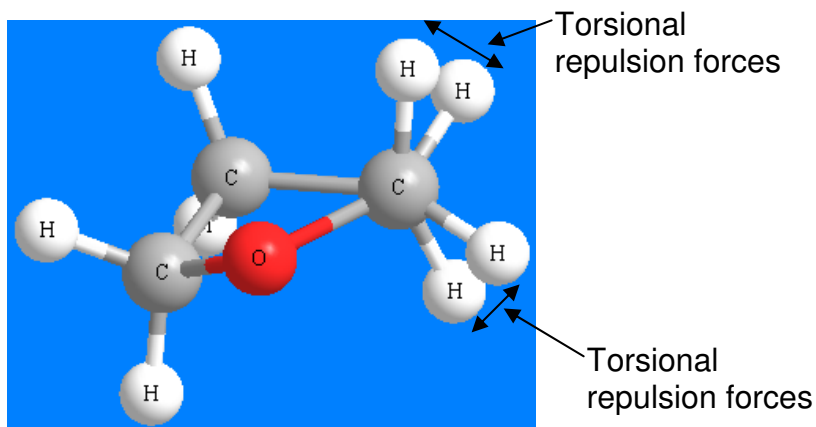


Figure 4.2 Torsional repulsion between hydrogen atoms in THF ring



The ring opening homopolymerization of tetrahydrofuran is typically conducted at 0-30 °C in the presence of Lewis acids or Bronsted superacids<sup>32</sup> to generate PTHF with molecular weight in the range of 600 Da to 3000 Da. Generally, the yield of THF homopolymerization is in the range of 65-75% because of the equilibrium between propagation and depropagation steps during the polymerization of THF. The polymerization equilibrium is based on the concurrence between S<sub>N</sub>2 nucleophilic attack of the monomer oxygen atom (propagation reaction) and the nucleophilic attack of the oxygen atom of a neighbouring repeating unit in the polymer chain (depropagation reaction by 'back biting') as shown in Figure 4.3. This homopolymerization reaction mechanism is known as an 'activated chain end' mechanism.<sup>99</sup>

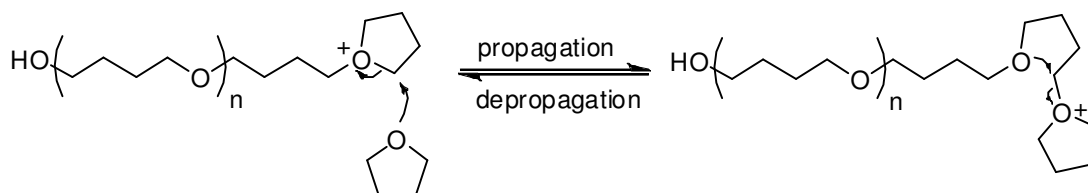


Figure 4.3 THF homopolymerization equilibrium step

The cationic ring opening of THF can also be conducted in the presence of alkylene oxide such as ethylene oxide (EO) and propylene oxide (PO) to generate copolymers of PTHF-EO and PTHF-PO respectively, which have molecular weights in the range of 3000 Da to 5000 Da. This copolymerization of THF with EO or PO is usually initiated by diols such as 1,4-butanediol<sup>100</sup> (Figure 4.4).

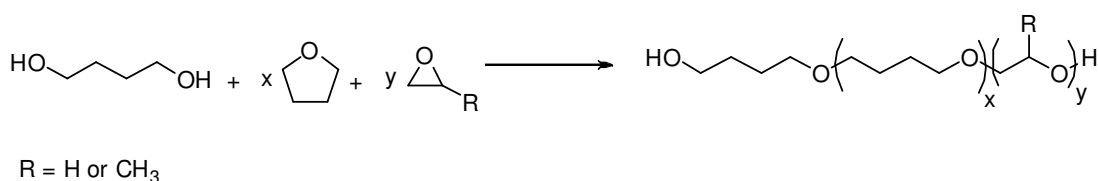


Figure 4.4 Copolymerization of THF with EO or PO initiated by 1,4-butanediol

The advantages of copolymerizing THF with EO or PO is the higher yield of polymers achievable (85-90%)<sup>101</sup> by this method as compared to homopolymerization. This is due to the suppression of the equilibrium characteristic of homopolymerization of THF by the presence of EO or PO as the mechanism for the copolymerization reaction is different from homopolymerization and is known as ‘activated monomer’ mechanism. In the reaction system there are two types of activated monomers namely activated oxirane (**4.1**) and activated THF (**4.2**). The activated monomer (**4.2**) was produced from nucleophilic attack on (**4.1**) by THF (Figure 4.5).<sup>102</sup>

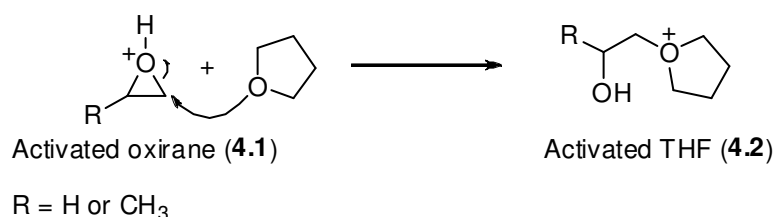


Figure 4.5 Activated monomers in the copolymerization reaction

The statistical copolymerization of THF with EO or PO by ‘activated monomer’ mechanism can be characterized by the following reactions (**RN1**, **RN2**, **RN3** and **RN4**; Figure 4.6). These reactions are the main reactions during the initiation and propagation of the copolymerization reaction.<sup>102</sup> The hydroxyl groups generated in **RN1** and **RN3** will be able to perform another nucleophilic attack on another activated monomer to propagate the copolymerization reaction.

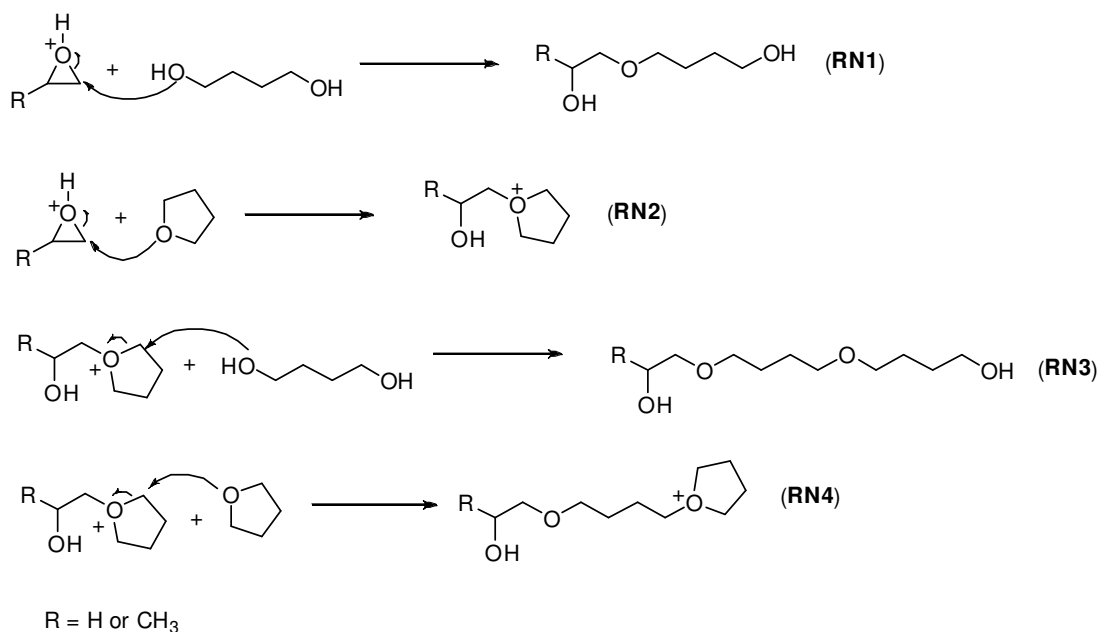


Figure 4.6 Reactions occurring during copolymerization of THF with EO or PO initiated by 1,4-butanediol

It was reported that copolymers of THF and EO or PO are used especially for the production of elastomeric PU that exhibited better elastic properties (elongation, tensile strength and modulus) as compared to PU elastomers derived from PO homopolymers or PO-EO copolymers.<sup>4</sup>

In view of the superior properties of PU elastomers derived from THF-EO or PO copolymers, this section intends to investigate the properties of PU elastomers derived from copolymers of THF with renewable epoxidized compounds, in which the EO and PO was substituted with renewable epoxidized plant oils.

The epoxidized plant oils prepared in Chapter 2 namely (2.3), (2.16), (2.17), (2.13) and (2.6) were used as the renewable epoxidized compounds in the copolymerization reaction with THF. In addition, euphorbia oil (2.18) was also included in this study,

which is a naturally occurring unsaturated plant oil with epoxide functionality (Figure 4.7).

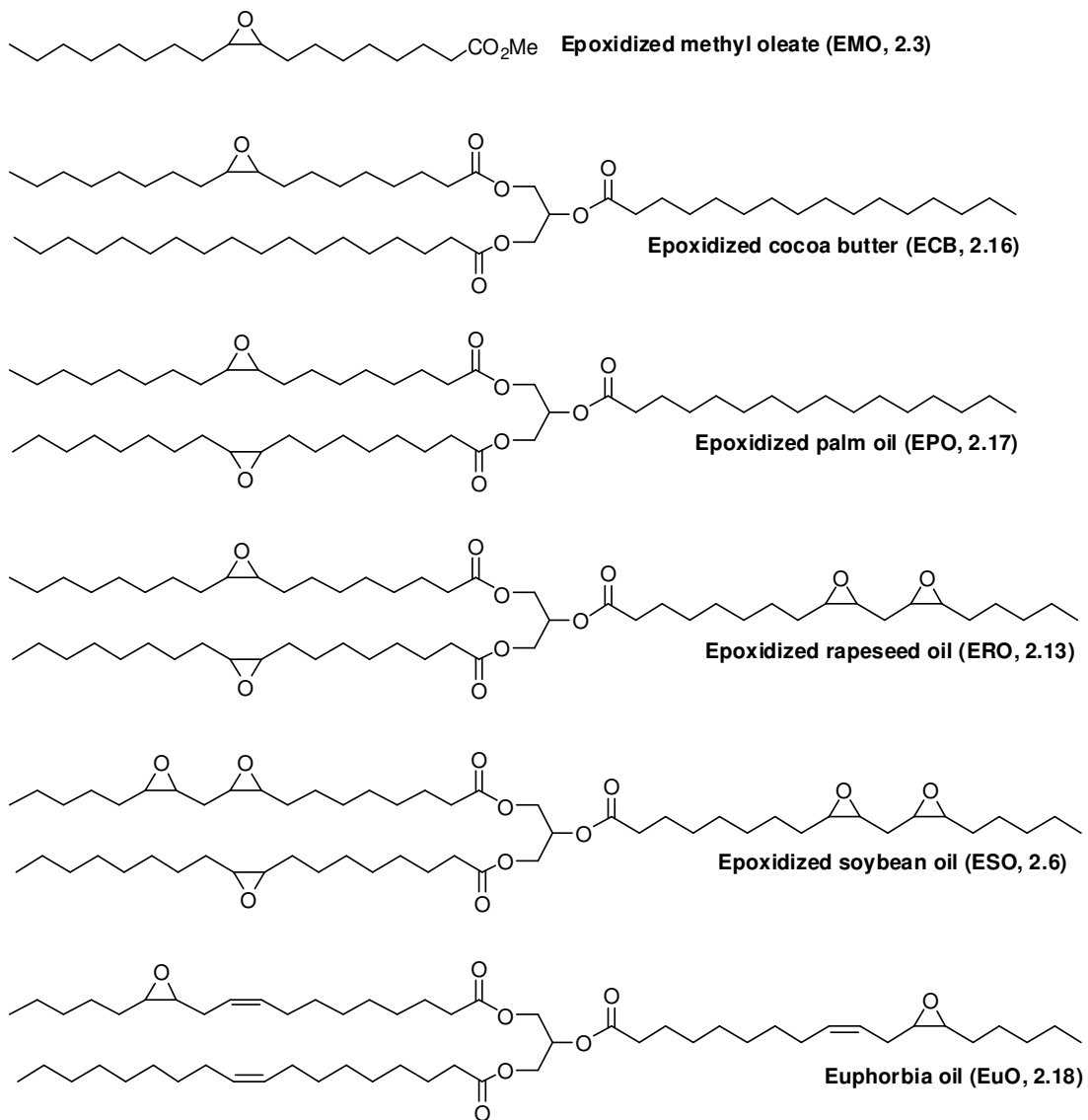


Figure 4.7 Epoxidized plant oils

## 4.1 SCREENING OF CHEMICAL COMPOUNDS AS POTENTIAL CATALYSTS

According to literature, the copolymerization of THF with EO and PO were catalyzed by Lewis acids ( $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{SnCl}_4$ )<sup>32</sup> or superacids ( $\text{HBF}_4$ ,  $\text{ClSO}_3\text{H}$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ).<sup>103</sup> Based on these literature, the same chemical compounds were screened in order to determine whether these reported chemical compounds can effectively catalyze the copolymerization of epoxidized plant oils and THF.

In addition, relatively weaker acids (trifluoroacetic acid, sulfuric acid) and other Lewis acids ( $\text{TiCl}_4$ ,  $\text{FeCl}_3$ ) were also screened as potential catalyst. The screening of catalyst was conducted with (**2.17**) as the renewable resources at 20 °C (Figure 4.8) to yield copolymers of (**2.17**) and THF (**EPO-THF**, **4.3**). The results of this screening study were tabulated in Table 4.1

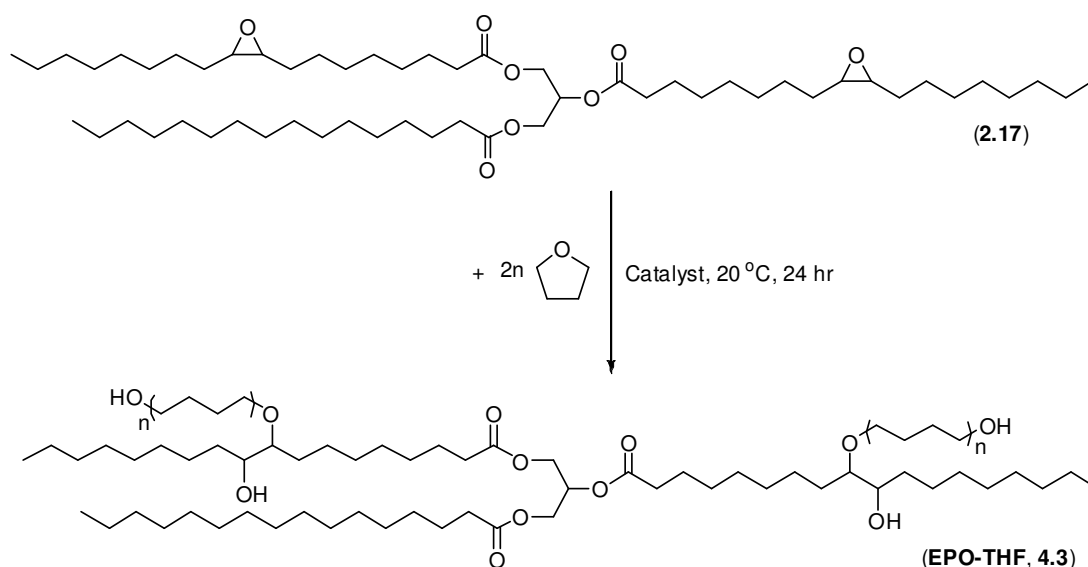


Figure 4.8 Copolymerization of (**2.17**) with THF

Table 4.1 Screening of chemical compounds as potential catalyst

Chemical compound	Mol equivalent of chemical	Polymer content (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
BF <sub>3</sub> .EtO <sub>2</sub>	0.02	97	282000	44100	6.39
FeCl <sub>3</sub>	0.1	90	45200	17400	2.60
SnCl <sub>4</sub>	0.1	93	111000	25200	4.40
AlCl <sub>3</sub>	0.1	0	-	-	-
TiCl <sub>4</sub>	0.1	0	-	-	-
HBF <sub>4</sub>	0.02	95	85000	22500	3.78
CF <sub>3</sub> SO <sub>3</sub> H	0.1	92	165000	35700	4.62
ClSO <sub>3</sub> H	0.1	0	-	-	-
CF <sub>3</sub> CO <sub>2</sub> H	0.1	0	-	-	-
H <sub>2</sub> SO <sub>4</sub>	0.1	0	-	-	-

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

The analysis of the copolymers produced from reactions was conducted with gel permeation chromatography (GPC) and was calibrated with polymethacrylate polymers. The GPC analysis of the monomer (**2.17**) indicated a number average molecular weight (M<sub>n</sub>) of about 1500 Da.

Out of the five evaluated Lewis acids, only three of the Lewis acids (BF<sub>3</sub>.EtO<sub>2</sub>, FeCl<sub>3</sub> and SnCl<sub>4</sub>) yielded the desired copolymers when (**2.17**) was used. On the other hand, two out of the three superacids (HBF<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H) were able to catalyze the copolymerization of (**2.17**) with THF. Meanwhile, the relatively weak acids (CF<sub>3</sub>CO<sub>2</sub>H and H<sub>2</sub>SO<sub>4</sub>) were not able to catalyze the reaction.

For all the acids that were able to catalyze the copolymerization reaction ( $\text{BF}_3\cdot\text{EtO}_2$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{HBF}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$ ), a control reactions for each acids was conducted, where the copolymerization reaction in Figure 4.8 was conducted using the same protocols but without (**2.17**) (Figure 4.9). The experimental results shows that ring opening polymerization of THF catalyzed by these acids do not happen without (**2.17**) as they failed to get any oligomeric or polymer material and end up with the starting material. This indicates that the (**2.17**) was needed for the ring opening polymerization of THF under reaction condition in Figure 4.8.

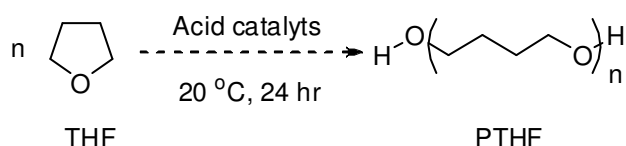


Figure 4.9 Control reactions of ring opening polymerization of THF with acid catalyts

Referring to Table 4.1, two boron based compounds ( $\text{BF}_3\cdot\text{EtO}_2$  and  $\text{HBF}_4$ ) were used at lower amounts (0.02 mol equivalent per mol of epoxide group) compared to other acids (0.1 mol equivalent) because when both boron based compounds were used at higher amounts (0.1 mol equivalent), the resultant copolymers were cross-linked (gelled) polymers, which were difficult to characterize. Based on the results in Table 4.1, both boron based acids were found to be better catalysts for the copolymerization of (**2.17**) with THF because lower catalyst loading was possible. Furthermore,  $\text{BF}_3\cdot\text{Et}_2\text{O}$  was chosen as the catalyst for the copolymerization of epoxidized plant oils with THF for further studies because it can produced copolymers with higher molecular weight.

## 4.2 COPOLYMERS OF EPOXIDIZED METHYL OLEATE AND TETRAHYDROFURAN

The epoxidized methyl oleate (**EMO**, **2.3**) was copolymerized with THF and boron trifluoride etherate as the catalyst at room temperature to yield copolymers (**EMO-THF**, **4.4**) (Figure 4.10). The following are the properties of the copolymers (**4.4**) tabulated in Table 4.2

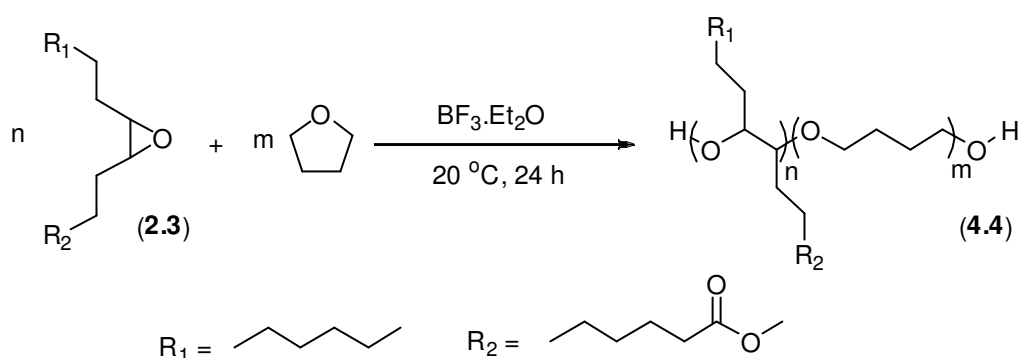


Figure 4.10 Copolymerization of (**2.3**) with THF

Table 4.2 Properties of (**4.4**)

Entry	Mol equivalent of $BF_3 \cdot Et_2O$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.01	0	-	-	-
2	0.025	75	17700	8500	2.08
3	0.05	97	54200	26100	2.07

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

GPC analysis was conducted on the produced copolymers with (**2.3**) as a standard, which indicated a  $M_n = 500$  Da. Referring to Table 4.2, the optimum amount of catalyst needed to give good yield of copolymers (**4.4**) was 0.05 mol equivalent of



BF<sub>3</sub>·Et<sub>2</sub>O per mol epoxide of **(2.3)** (Entry 3), which gave 97% copolymers **(4.4)** that have a number average molecular weight ( $M_n$ ) of 26100 Da. Lower yield of copolymers was obtained with lower catalyst loading and when the reaction was conducted with 0.01 mol equivalent of catalyst only starting material was recovered. MALDI-TOF-MS analysis confirmed that **(4.4)** (Figure 4.11) was a copolymer with a molecular weight up to 3000 Da. The peak at 664 Da corresponds to **(4.5)**, a sodium adduct of **(2.3)** dimer (Figure 4.12) and the peak at 1817 Da corresponds to **(4.6)**, a sodium adduct of **(4.5)** with 17 repeating units of ring opened THF (Figure 4.13)

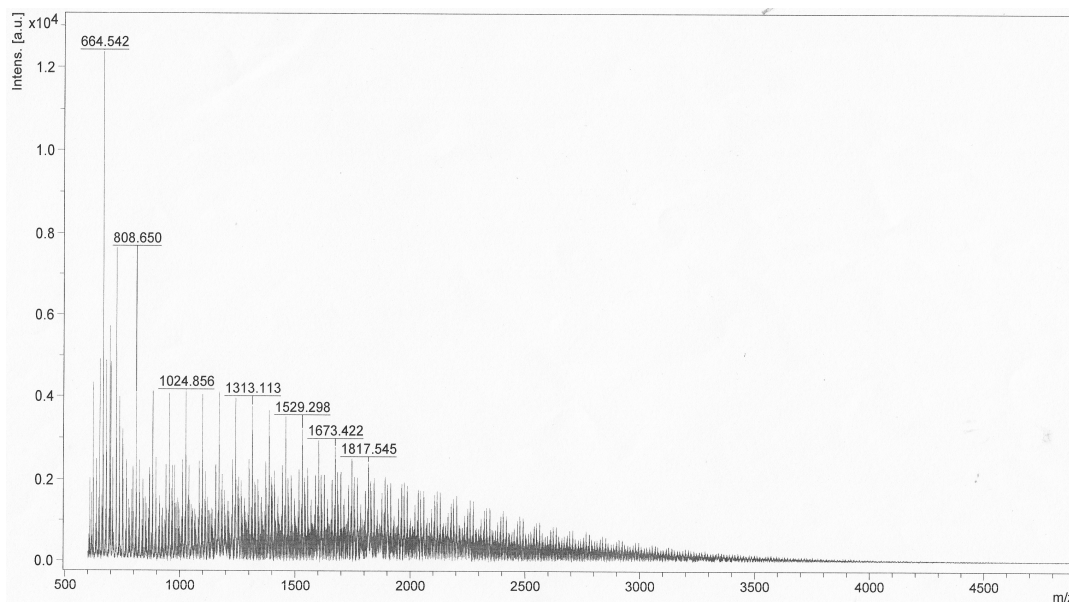


Figure 4.11 MALDI-TOF-MS spectrum of **(4.4)** by using DHB as the matrix in the analysis

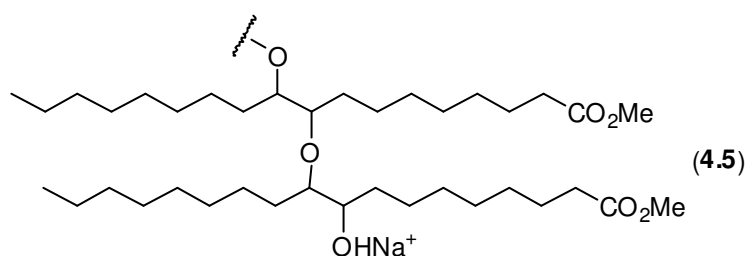


Figure 4.12 Dimer of **(2.3)**

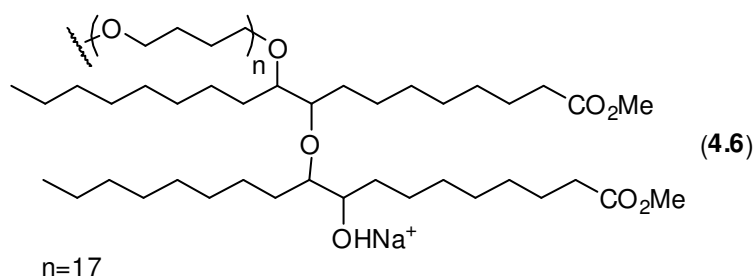


Figure 4.13 Dimer of (2.3) with 17 repeating units of ring opened THF

Figure 4.14 shows the stacked 400 MHz  $^1\text{H}$  NMR spectrum of (2.3) and (4.4). Referring to the  $^1\text{H}$  NMR spectrum, the epoxide group of (2.3) at 2.80-3.15 ppm was ring opened to copolymerize with THF yielding ether and hydroxyl functionalities (3.51-3.60 ppm) and peaks corresponding to ring opened THF [1.56-1.66 ppm (peak b) and 3.35-3.45 ppm (peak a)].

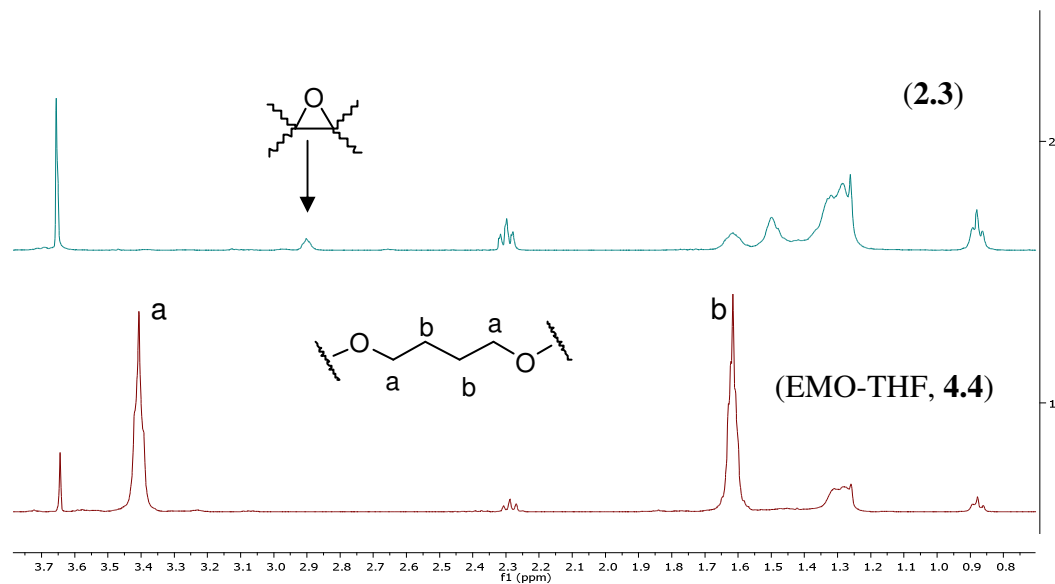


Figure 4.14 Stacked 400MHz  $^1\text{H}$  NMR spectrum of (2.3) and (4.4) in  $\text{CDCl}_3$ .

### 4.3 COPOLYMERS OF EPOXIDIZED COCOA BUTTER AND TETRAHYDROFURAN

The copolymerization of epoxidized cocoa butter (**ECB**, **2.16**) and THF was conducted using the same method as for (**2.3**) (Figure 4.15). The properties of the copolymers (**ECB-THF**, **4.7**) are tabulated in Table 4.3

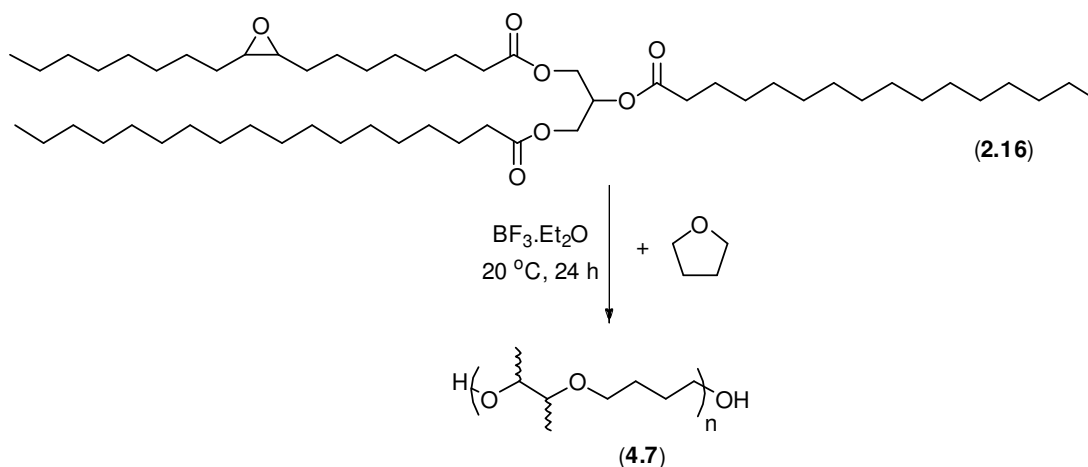


Figure 4.15 Copolymerization of (**2.16**) with THF

Table 4.3 Properties of (**4.7**)

Entry	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.02	0	-	-	-
2	0.05	82	37100	16500	2.25
3	0.1	93	83200	29600	2.81

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

The optimum catalyst loading for copolymerization of (**2.16**) with THF was 0.1 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , which yielded 93 % (Entry 3) of copolymers (**4.7**). Lower

amount of catalyst gave lower yields of copolymers and lower  $M_n$ . Catalyst loading at 0.02 mol equivalent of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was not sufficient to catalyze the reaction.

MALDI-TOF-MS analysis of **(4.7)** (Figure 4.16) confirmed the copolymerization of **(2.16)** with THF, in which the peak at 1116 Da corresponds to the sodium adduct of **(2.16)** plus 3 units of THF **(4.8)** (Figure 4.17). Furthermore, the peak at 1920 Da corresponds to dimer of **(2.16)** plus 2 units of THF **(4.9)** (Figure 4.17).

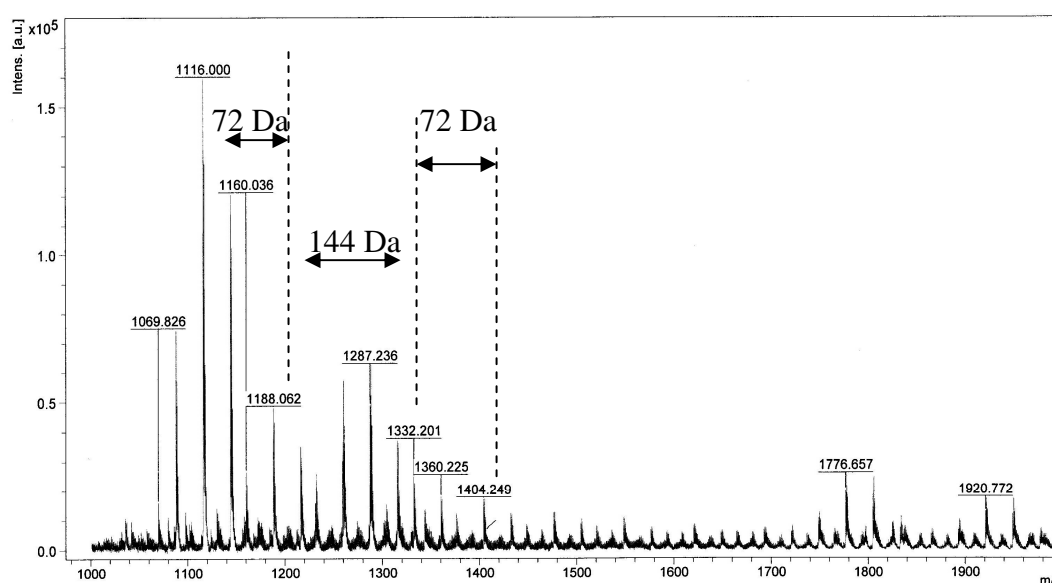


Figure 4.16 MALDI-TOF-MS spectrum of **(4.7)** by using DHB as the matrix in the analysis

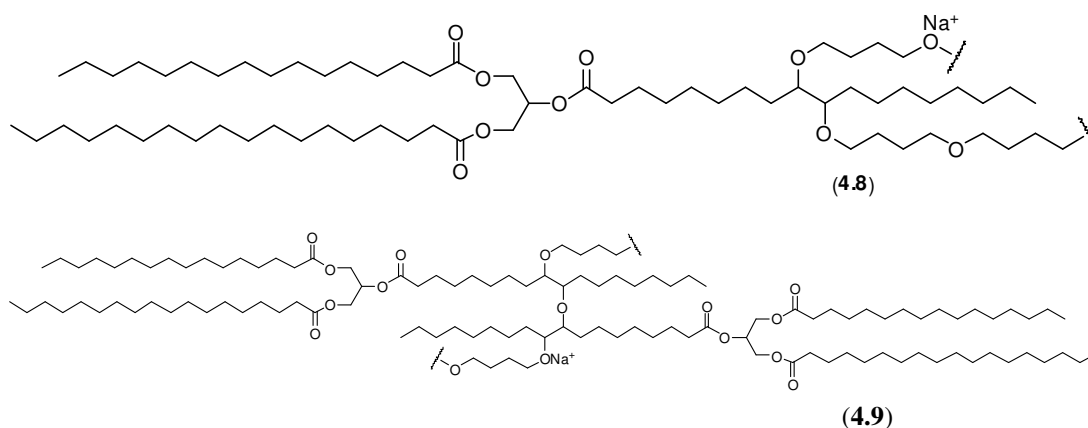


Figure 4.17 Copolymers of **(2.16)** with THF

The stacked 400 MHz  $^1\text{H}$  NMR spectrum of (**2.16**) and (**4.7**) (Figure 4.18) shows that the epoxide group of (**2.16**) at 2.78-3.05 ppm was ring opened to copolymerize with THF similar to (**2.3**).

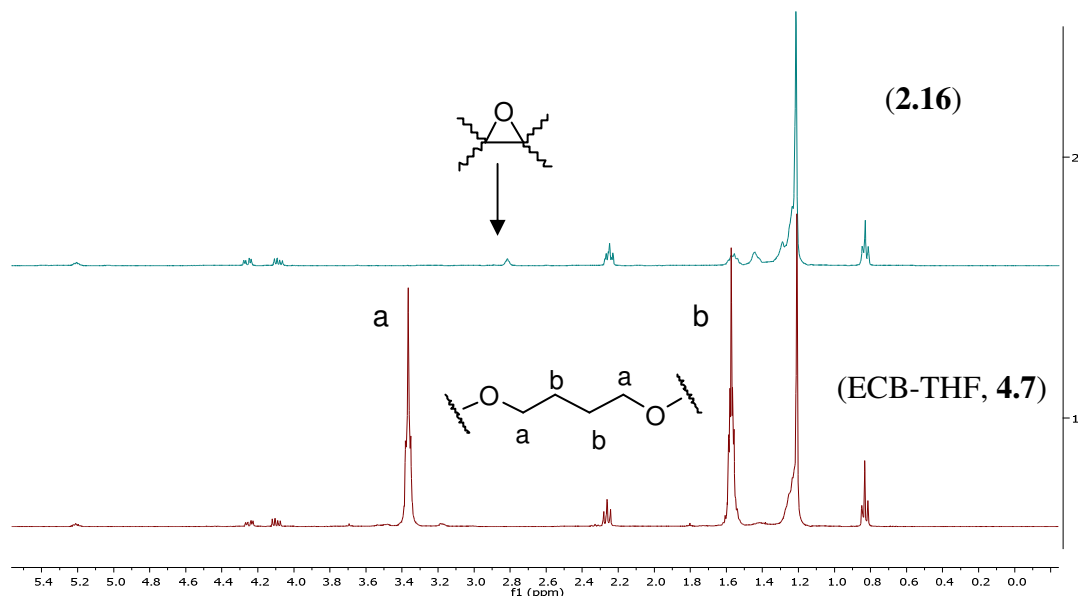


Figure 4.18 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of (**2.16**) and (**4.7**) in  $\text{CDCl}_3$ .

#### 4.4 COPOLYMERS OF EPOXIDIZED PALM OIL AND TETRAHYDROFURAN

The copolymerization of epoxidized palm oil (**2.17**) and THF was conducted in the same way as epoxidized cocoa butter (**2.17**) (Figure 4.19) and the products (**4.10**) were analyzed by GPC, MALDI-TOF-MS and  $^1\text{H}$  NMR as before. The properties of the copolymers (EPO-THF, **4.10**) are tabulated in Table 4.4

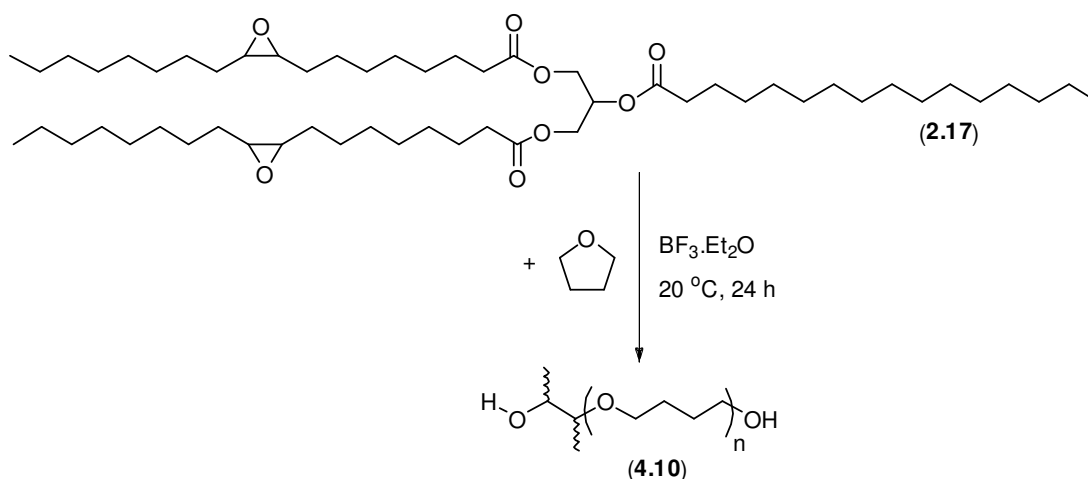


Figure 4.19 Copolymerization of (2.17) with THF

Table 4.4 Properties of (4.10)

Entry	Mol equivalent of $\text{BF}_3\cdot\text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
			$M_w$ (Da)	$M_n$ (Da)	PDI
1	0.005	0	-	-	-
2	0.01	80	147000	44800	3.28
3	0.02	97	366000	55800	6.56
4	0.03	Gelled	-	-	-

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

Referring to Table 4.4, the optimum catalyst loading was 0.02 mol equivalent of  $\text{BF}_3\cdot\text{Et}_2\text{O}$ , in which we were able to achieve about 95% yield of copolymers that have a number average molecular weight of about 56,000 Da. Catalyst loading at 0.005 mol equivalent was not sufficient to catalyze the reaction, while catalyst loading at 0.03 mol equivalent yielded cross-linked polymers, which indicates that higher amounts of catalyst generated more active polymer chains that promoted cross-linking during polymerization. This prompted the study on the effect of other

reaction parameters (monomer ratio, temperature and duration) on the properties of copolymers

#### 4.5 EFFECT OF MONOMER RATIO ON THE PROPERTIES OF COPOLYMERS

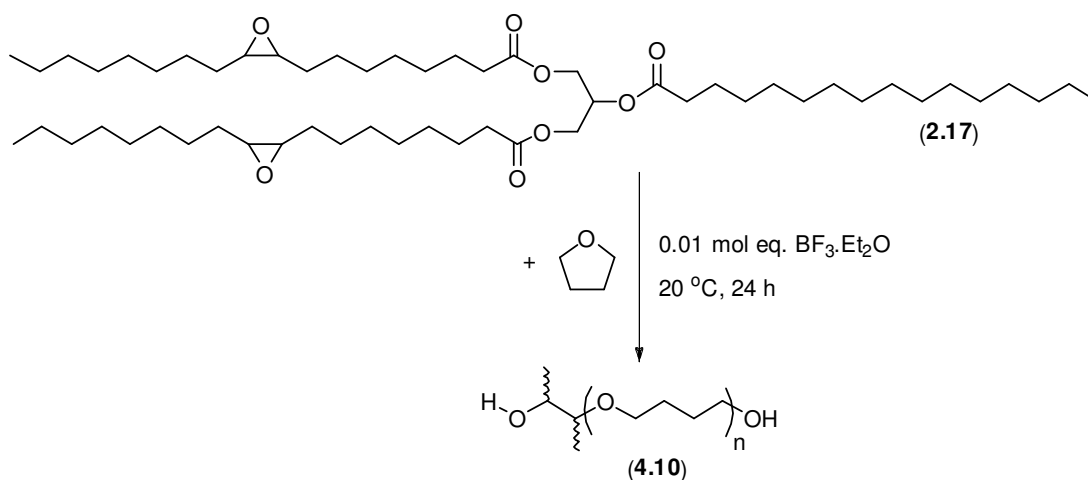


Figure 4.20 Copolymerization of (**2.17**) with THF on different monomer ratio

For this study, epoxidized palm oil (**2.17**) was used as the renewable epoxidized plant oil to copolymerize with THF (Figure 4.20). The ratio between (**2.17**) and THF was varied in order to observe changes in the properties of the copolymers (**4.10**). The following Table 4.5 displays the properties of the copolymer from this study.

Table 4.5 Properties of **(4.10)** from different monomer ratio

Entry	Monomer ratio THF : <b>(2.17)</b> (ml : g)	Yield (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	4 : 1	Gelled	-	-	-
2	8 : 1	Gelled	-	-	-
3	12 : 1	Gelled	-	-	-
4	16 : 1	79	147000	44800	3.28
5	20 : 1	81	173000	56000	3.09
6	24 : 1	83	169000	56100	3.01

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

The results in Table 4.5 shows that the minimum ratio between THF and **(2.17)** must be equal to or above the 16 : 1 ratio (Entry 4) in order to get non-cross-linked (liquid) product. Below the specific ratio, we achieved cross-linked copolymers (Entry 1 to 3). Higher ratios of THF to **(2.17)** (Entry 5 and 6) yielded copolymers with higher number average molecular weight as compared to copolymer from Entry 4.

It is proposed that the cross-linking of copolymers (Entry 1 to 3) was due to the higher amount of **(2.17)** presence in the monomers mixture. Results from section 2.5, (page 71) show that **(2.17)** will form cross-linked polymers if it was ring opened with BF<sub>3</sub>.Et<sub>2</sub>O without solvent. However, it will form liquid oligomeric polyols if it was ring opened in solvent. In other word, it needs solvent to prevent the formation of cross-linked products. In this copolymerization reaction system, THF acts as a monomer as well as a solvent for the reaction system. Therefore, at lower THF : **(2.17)** ratios (Entry 1 to 3), the amount of THF was not sufficient to prevent the



cross-linking of (2.17). At higher THF ratios (Entry 4 to 6), the amount of THF as solvent was sufficient to prevent/retard cross-linking of the copolymers.

Higher amounts of THF in the reaction mixture also yielded copolymers with higher molecular weights. This suggests that reaction RN4 (Figure 4.6) is now dominating the reaction pathway. Furthermore, the presence of THF in the reaction system activated the epoxy ring opening reaction because the amount of catalyst needed ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) (0.01 mol equivalent) for getting high yields of polymer was comparatively lower than similar epoxy ring opening reaction conducted without THF in n-hexane (0.035 mol equivalent). In other words, it takes less amount of catalyst to cause gelation in reaction conducted in THF than a reaction conducted in n-hexane.

#### **4.6 EFFECT OF REACTION TEMPERATURE ON THE PROPERTIES OF THE COPOLYMERS**

The copolymerization of (2.17) with THF was repeated at different temperature to evaluate the effect of temperature on the properties of the copolymers (4.10). The following Table 4.6 tabulates the result of this study.

Table 4.6 Properties of **(4.10)** from copolymerization at different temperature

Entry	Temperature (°C)	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
				M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	60	0.025	80	62900	16500	3.81
2	20	0.025	Gelled	-	-	-

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

When the reaction was conducted at 60 °C with 0.025 mol equivalent of BF<sub>3</sub>.Et<sub>2</sub>O (Entry 1), the product was liquid copolymers (80% yield) with an average molecular weight (M<sub>n</sub>) of 16500. However, by lowering the reaction temperature to 20 °C (Entry 2), the product was a cross-linked (gelled) copolymer.

Results from Chapter 2 show that gelation occurs during homopolymerization of **(2.17)** catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O (page 71) and this occurred through cross-linking of epoxide. The same cross-linking of epoxide caused the gelation in the copolymerization of **(2.17)** and THF at 20 °C. This is due to the lower activation energy for epoxide ring opening (20 kcal/mol)<sup>104</sup> as compared to THF ring opening (51.3 kcal/mol).<sup>116</sup> Therefore, when the copolymerization was conducted at low temperature (20 °C), the epoxide ring opening reaction predominates thus causing gelation but when the reaction was conducted at higher temperature (60 °C), the THF ring opening reaction predominates yielding liquid copolymers.

#### 4.7 THE EXTENT OF COPOLYMERIZATION REACTION AGAINST TIME

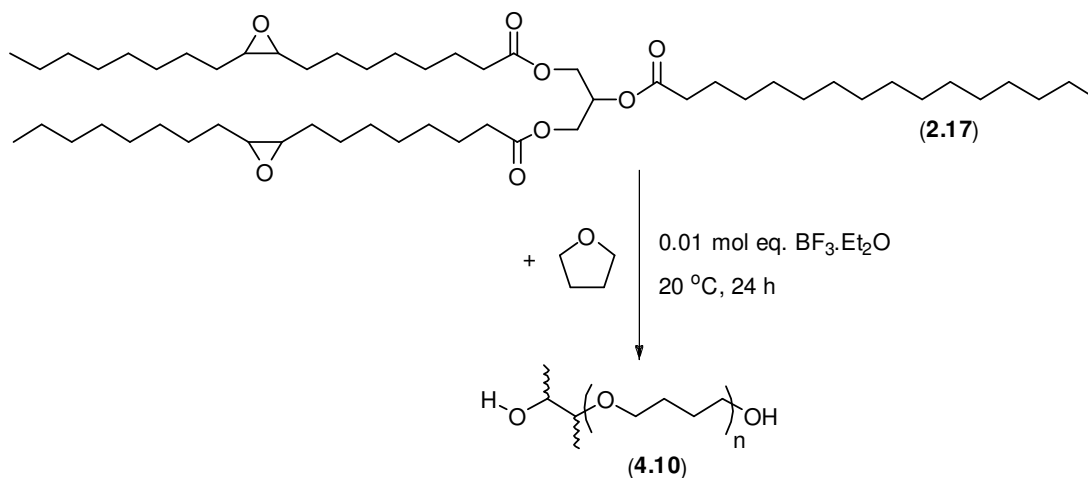


Figure 4.21 Copolymerization of **(2.17)** with THF

A study was conducted to evaluate the extent of copolymerization reaction of **(2.17)** with THF catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  against time (Figure 4.21). A small aliquot was removed from the reaction mixture after 5 minutes and 30 minutes of reaction and then at every hour of reaction. The small sample was washed with water to quench the reaction before analyzing it with GPC. The following Table 4.7 and Figure 4.22 show the result of this study.

Table 4.7 The extent of copolymerization of **(2.17)** with THF catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  against time

Reaction time (minutes)	Polymer content (%)	Gel permeation chromatography		
		$M_w$ (Da)	$M_n$ (Da)	PDI
5	2	27900	26500	1.05
30	22	50800	32300	1.57
60	37	64000	36100	1.77
120	54	87800	40800	2.15
240	65	112000	46300	2.41
480	73	150000	48600	3.09
720	78	181000	53800	3.36
1440	82	234000	58700	3.99

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

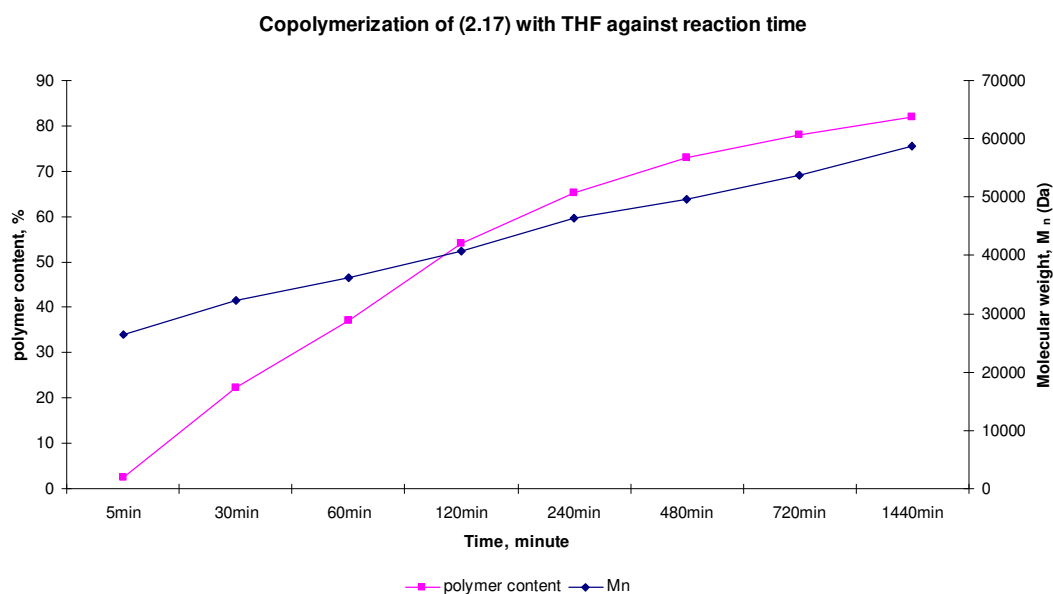


Figure 4.22 Graph to show the copolymerization of **(2.17)** with THF against time

Referring to Table 4.7, after 5 minutes into the reaction, the amount of **(4.10)** was low (2%) but the  $M_n$  of **(4.10)** was significantly high (26500 Da). The copolymers content increased progressively with reaction time, in which it reached 82% in 24 hours and at the same time the PDI of the copolymers also broadens indicating more

polymer chains were cross-linking with the longer reaction time. Referring to Figure 4.20, the polymer content starts to level out (plateau), indicating that the polymer content will not increase significantly with a longer reaction time.

The number average molecular weight ( $M_n$ ) of **(4.10)** analyzed by GPC was about 58700 Da. MALDI-TOF-MS analysis of **(4.10)** (Figure 4.23) shows peak at 1086 Da, which correspond to sodium adduct of epoxide ring opened (**2.17**) plus 2 units of THF (**4.11**) (Figure 4.24). The other peaks in the spectrum were **(4.11)** plus additional units of THF (72 Da). The peak 1158 Da to 1246 Da is an additional 89 Da which is a unit of THF (72 Da) plus one hydroxyl group (-OH, 17 Da).

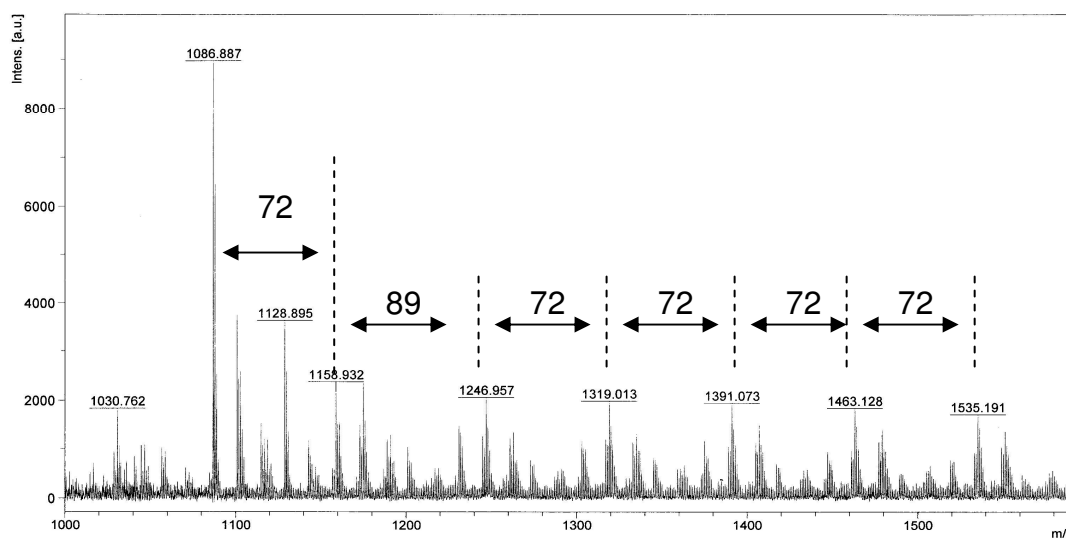


Figure 4.23 MALDI-TOF-MS spectrum of **(4.10)** by using DHB as the matrix in the analysis

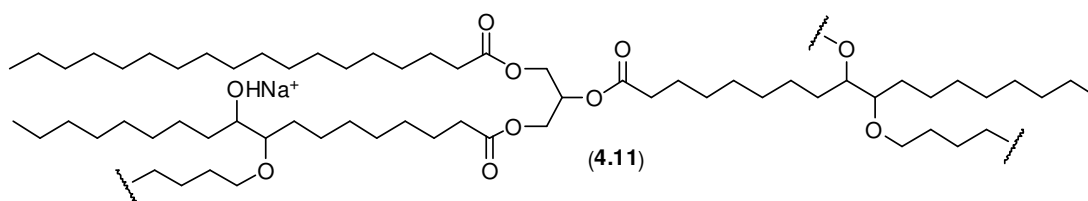


Figure 4.24 Copolymers of (4.11)

The reaction was also followed by  $^1\text{H}$  NMR and the following Figure 4.25 shows the stacked 400 MHz  $^1\text{H}$  NMR plot of copolymers (4.10) at 30 minute, 6 hours, 12 hours and 24 hours of reaction time.  $^1\text{H}$  NMR analysis shows that the epoxide group of (2.17) (2.80-3.10 ppm) diminishes with time as expected.

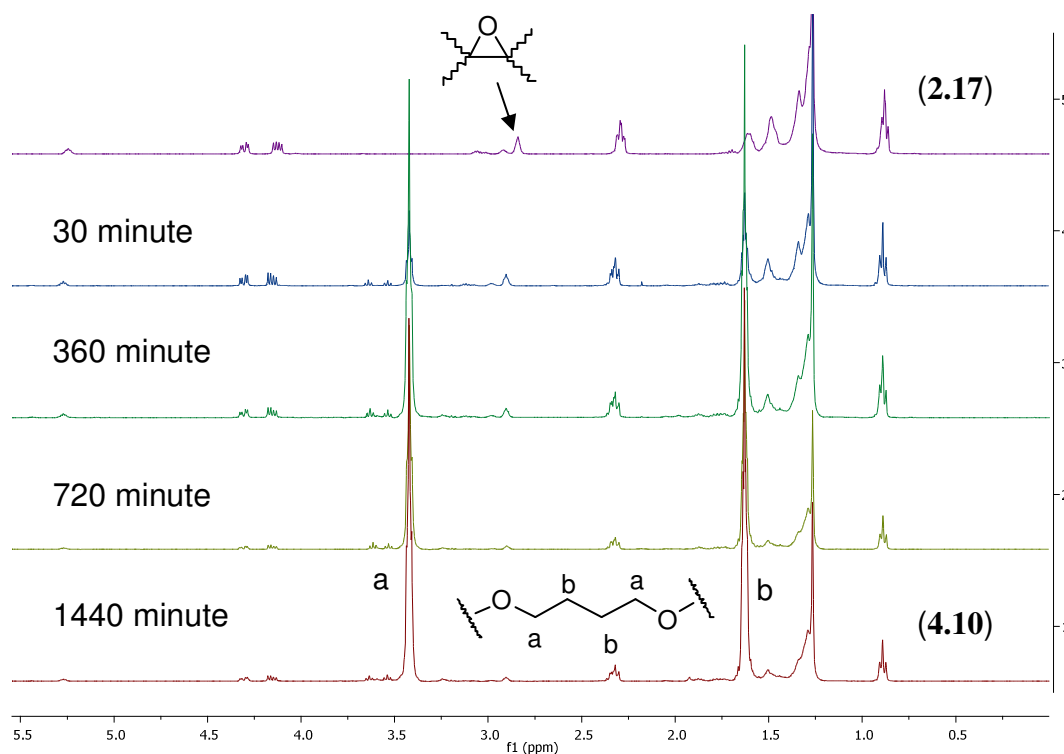


Figure 4.25 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of (2.17) and reaction mixture in  $\text{CDCl}_3$  at certain reaction time during copolymerization.

#### 4.8 COPOLYMERS OF EPOXIDIZED RAPESEED OIL AND TETRAHYDROFURAN

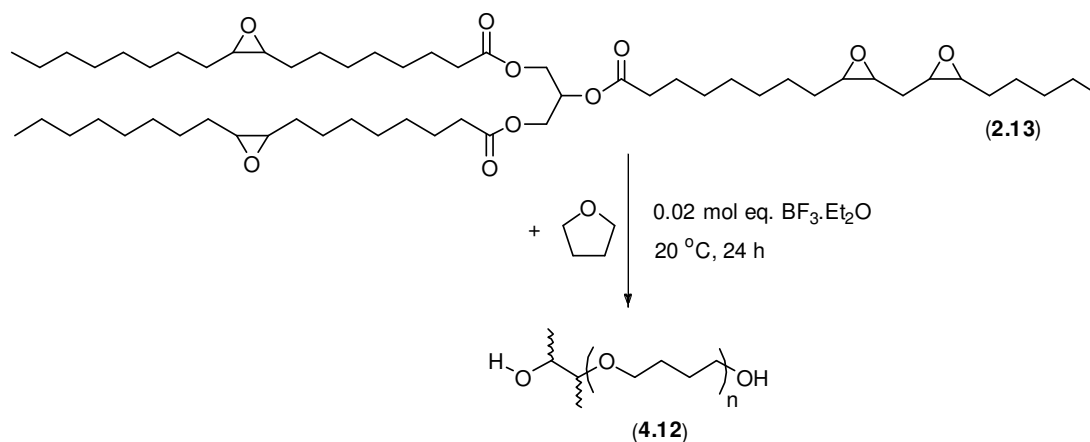


Figure 4.26 Copolymerization of (**2.13**) with THF

The copolymerization of epoxidized rapeseed oil (**2.13**) and THF was conducted in the same way as epoxidized cocoa butter (**2.16**) (Figure 4.26) in order to evaluate the effect of higher epoxide functionality on the properties of the copolymers. The products (**4.12**) were analyzed by GPC, MALDI-TOF-MS and  $^1\text{H}$  NMR as before and the properties of the copolymers (ERO-THF, **4.12**) are tabulated in Table 4.8

Table 4.8 Properties of (**4.12**)

Entry	Monomer ratio THF : ( <b>2.13</b> ) (g : ml)	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
				$M_w$ (Da)	$M_n$ (Da)	PDI
1	50 : 1	0.02	Gelled	-	-	-
2	80 : 1	0.02	95	229000	53900	4.25
3	100 : 1	0.02	97	276000	74300	3.71

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

In comparison to (**2.17**), the copolymerization of (**2.13**) needed more THF as solvent to prevent gelation of the reaction mixture, in which the ratio between THF and (ERO,X) must be at least 80 : 1 (THF : **2.13**) to yield liquid copolymers. When the ratio was 100 : 1 (THF : **2.13**), the yield of the copolymers was about 97% and the  $M_n = 74300$  Da.

MALDI-TOF-MS analysis of (**4.12**) (Figure 4.27) shows a peak at 1170 Da which corresponds to a ring opened (**2.13**) plus 3 units of THF (**4.13**), while peak at 1262 Da correspond to (**4.14**) (Figure 4.28). Subsequent peaks are (**4.14**) plus additional units of THF (72 Da) as shown in Figure 4.27.

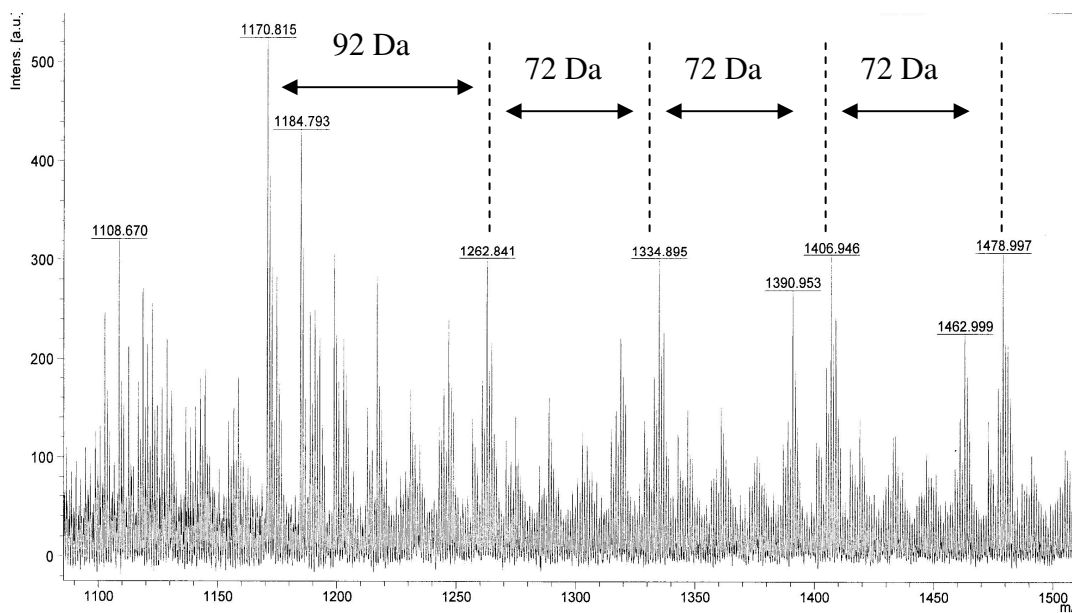


Figure 4.27 MALDI-TOF-MS spectrum of (**4.12**) by using DHB as the matrix in the analysis



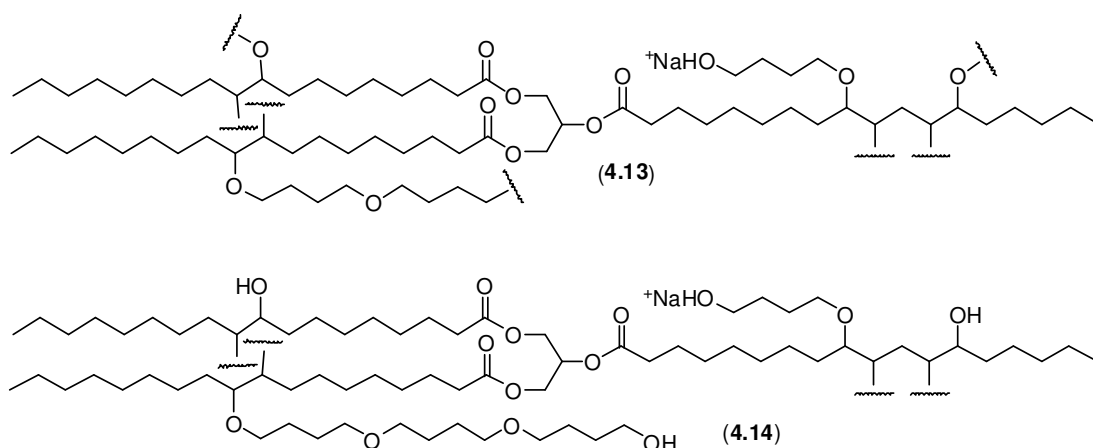


Figure 4.28 Copolymers of (2.13) and THF, (4.13) and (4.14)

The stacked 400 MHz  $^1\text{H}$  NMR spectrum of (2.13) and (4.12) (Figure 4.29) shows that the epoxide group of (2.13) at 2.84-3.22 ppm was ring opened to copolymerize with THF. The larger incorporation of THF to the copolymer can also be seen.

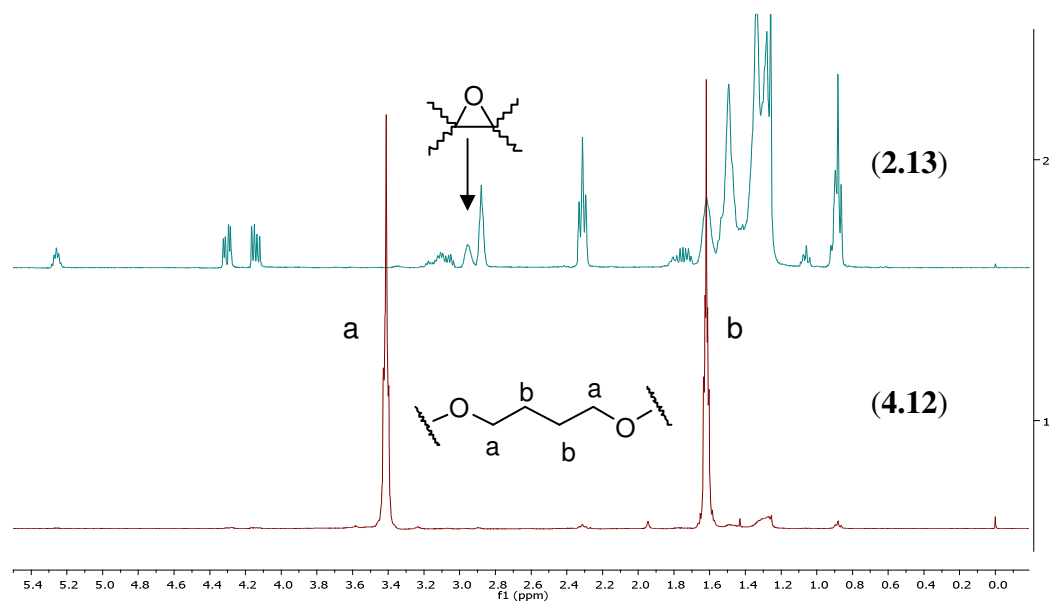


Figure 4.29 400 MHz  $^1\text{H}$  NMR spectrum of (2.13) and (4.12) in  $\text{CDCl}_3$

## 4.9 COPOLYMERS OF EPOXIDIZED SOYBEAN OIL AND TETRAHYDROFURAN

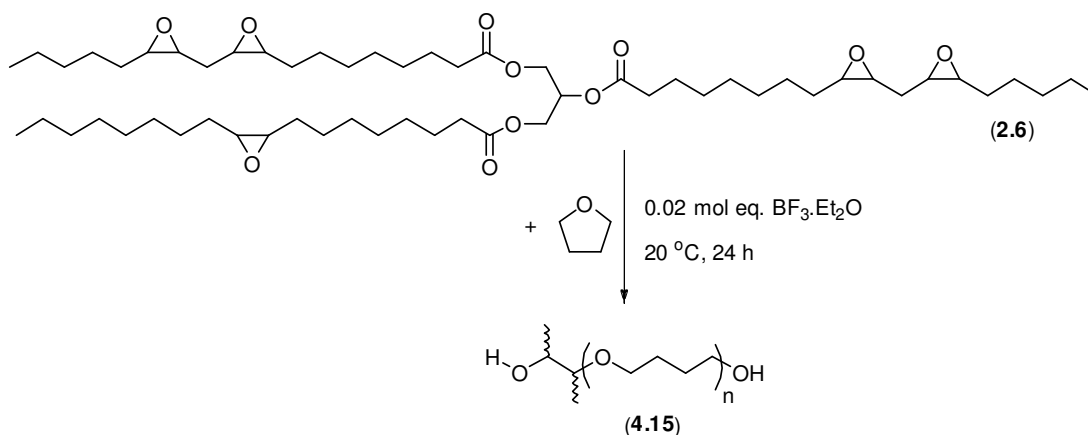


Figure 4.30 Copolymerization of (2.6) with THF

The copolymerization of epoxidized soybean oil (2.6) with THF was conducted in similar method as epoxidized rapeseed oil (2.13) (Figure 4.30).

Table 4.9 Properties of (4.15)

Entry	Monomer ratio THF : (2.6) (g : ml)	Mol equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Yield (%)	Gel permeation chromatography		
				$M_w$ (Da)	$M_n$ (Da)	PDI
1	50 : 1	0.02	Gelled	-	-	-
2	80 : 1	0.02	96	233000	57800	4.03
3	100 : 1	0.02	98	364000	115000	3.17

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

Similar to (2.13), the copolymerization of (2.6) needed more THF as solvent to prevent gelation of the reaction mixture, in which the ratio between THF and (2.6) must be at least 80 : 1 (THF : 2.6) to yield liquid copolymers. When the ratio was 100 : 1 (THF : 2.6), the yield of the copolymers was about 97% and the number

average molecular weight was about 115000 Da, which is higher than **(4.12)** because of the additional epoxide group of **(2.6)**.

MALDI-TOF-MS analysis of **(4.15)** (Figure 4.31) shows a peak at 1033 Da which corresponds to a ring opened **(2.6)** **(4.16)**, while peak at 1103 Da correspond to **(4.17)** (Figure 4.32). Subsequent peaks are **(4.17)** plus additional units of THF (72 Da) as shown in Figure 4.31.

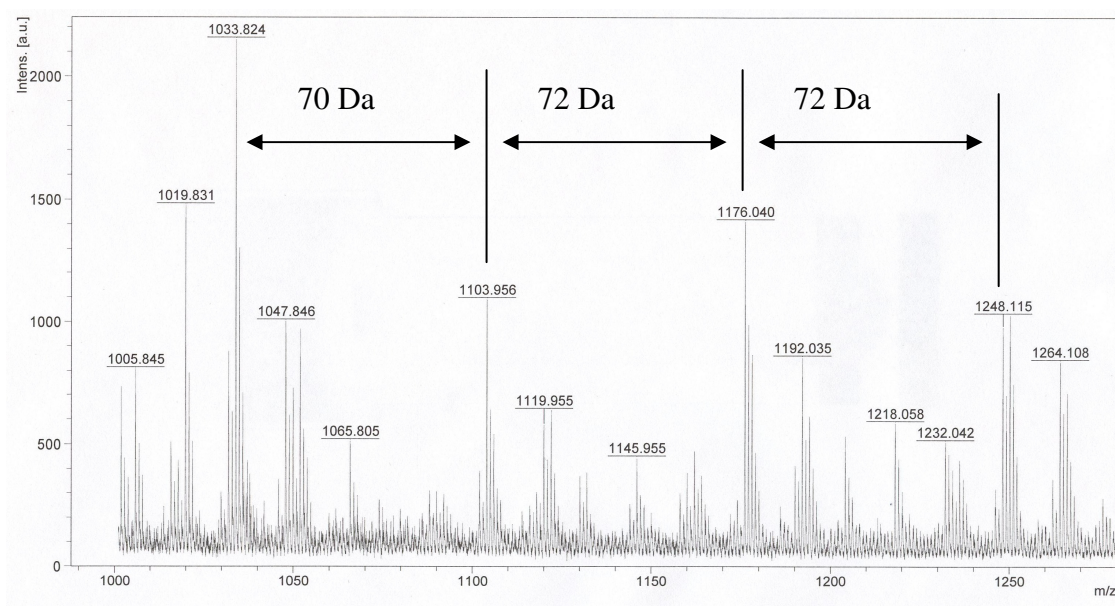


Figure 4.31 MALDI-TOF-MS spectrum of **(4.15)** by using DHB as the matrix in the analysis

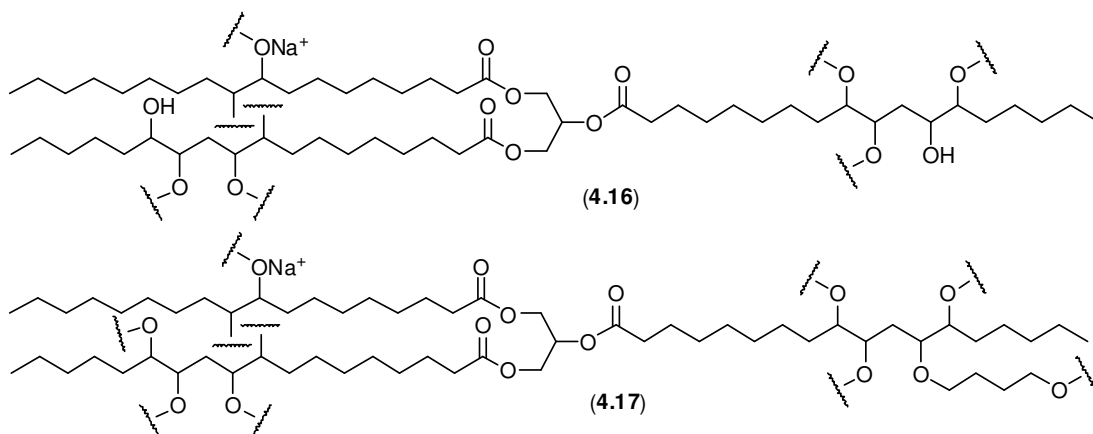


Figure 4.32 Copolymers of **(2.6)** and THF, **(4.16)** and **(4.17)**

Similarly to (4.12), the stacked 400 MHz  $^1\text{H}$  NMR spectrum of (2.6) and (4.15) shown below (Figure 4.33) shows the large amount of THF incorporated.

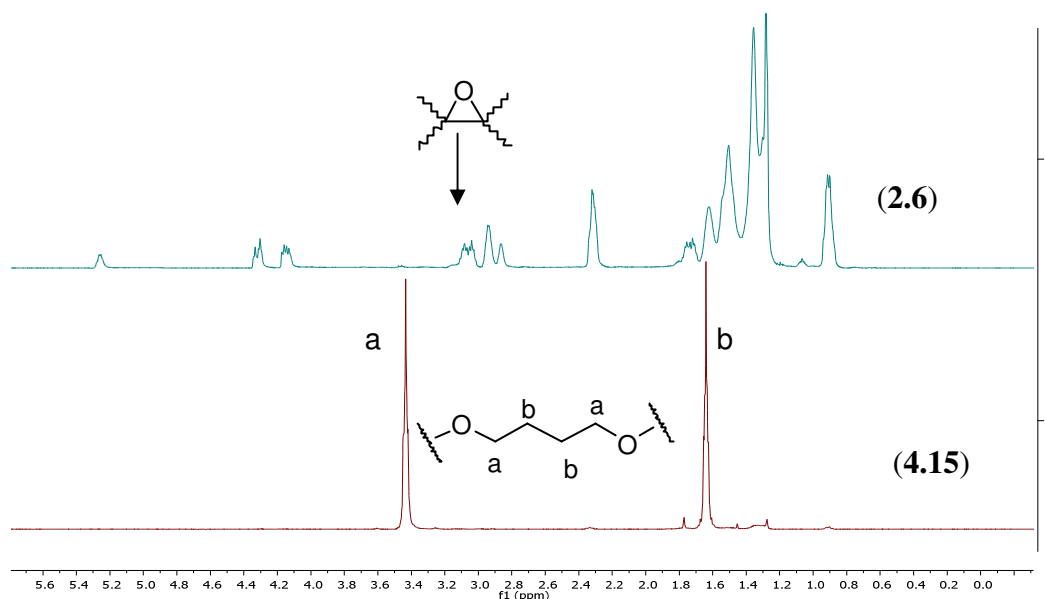


Figure 4.33 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of (2.6) and (4.15) in  $\text{CDCl}_3$

#### 4.10 COPOLYMERS OF EUPHORBIA OIL AND TETRAHYDROFURAN

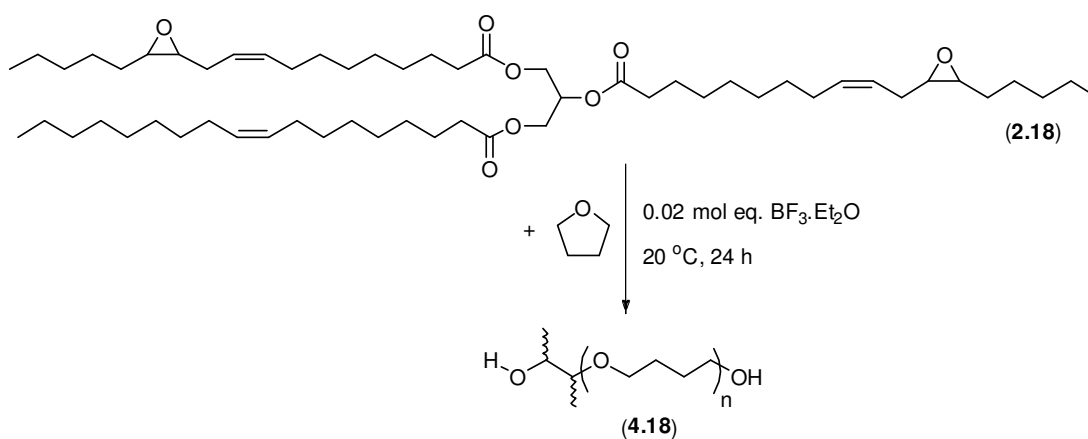


Figure 4.34 Copolymerization of (2.18) with THF

The copolymerization of euphorbia oil (**2.18**) with THF was conducted in similar method as epoxidized soybean oil (**2.6**) (Figure 4.34).

Table 4.10 Properties of (**4.18**)

Entry	Monomer ratio THF : ( <b>2.18</b> ) (g : ml)	Mol equivalent of BF <sub>3</sub> .Et <sub>2</sub> O	Yield (%)	Gel permeation chromatography		
				M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	20 : 1	0.02	Gelled	-	-	-
2	30 : 1	0.02	97	112000	33500	3.34

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

The liquid copolymers of (**2.18**) and THF can be produced at lower monomer ratio (THF : **2.18**) as compared to (**2.6**) due to the lower epoxide functionality of EuO. The optimum monomer ratio was 30 : 1, which yielded 97 % copolymers that have a average molecular weight of 33500 Da. The 400 MHz <sup>1</sup>H NMR spectrum of (**4.18**) shows similar peaks exhibited by previous plant oils and MALDI-TOF-MS analysis of (**4.18**) shows a peak at 1150 Da which corresponds to a (**4.19**), while peak at 1190 Da correspond to (**4.20**) (Figure 4.35).

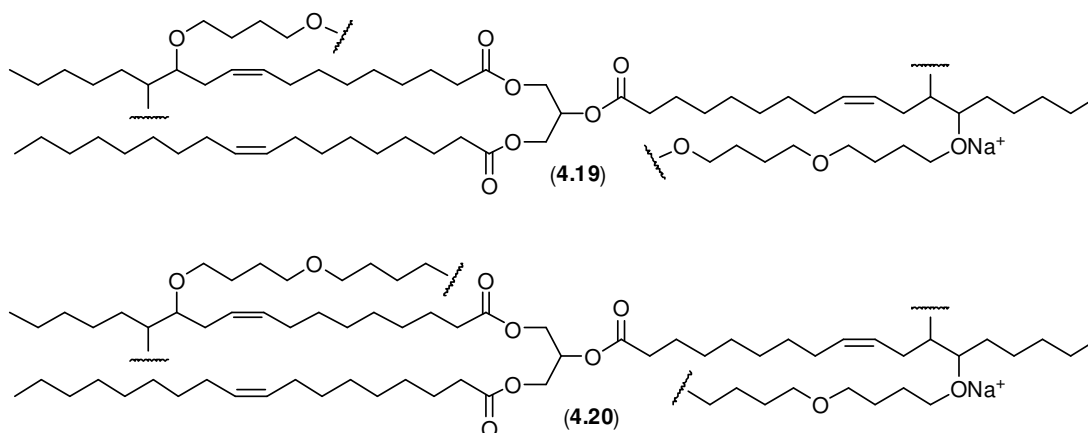
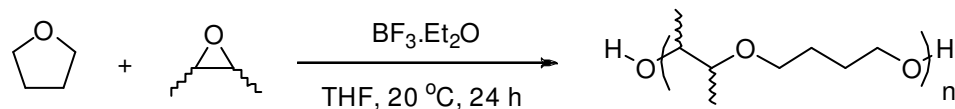


Figure 4.35 Copolymers of (**2.18**) and THF, (**4.19**) and (**4.20**)

#### 4.11 SUMMARY OF COPOLYMERIZATION OF EPOXIDIZED OILS AND TETRAHYDROFURAN



The following Table 4.11 shows the properties of copolymers of THF with epoxidized methyl oleate (**2.3**) and the 5 types of epoxidized plant oils (**2.16**, **2.17**, **2.13**, **2.6** and **2.18**). These copolymers were produced through the optimum reaction conditions (yield) found for each type of oils. The reaction products were analyzed by  $^1\text{H}$  NMR and GPC.

Table 4.11 Properties of copolymers from ring opened epoxidized oils and THF

EO	THF:EO	Mol eq.	Yield (%)	GPC			OHV	AV
				$M_w$ (Da)	$M_n$ (Da)	PDI		
<b>2.3</b>	20:1	0.05	97	54100	26100	2.07	25	7
<b>2.16</b>	5:1	0.1	93	83200	29600	2.80	27	1
<b>2.17</b>	30:1	0.02	97	366000	55800	6.56	40	1
<b>2.18</b>	30:1	0.02	97	112000	33500	3.33	33	1
<b>2.13</b>	100:1	0.02	97	276000	74300	3.71	48	1
<b>2.6</b>	100:1	0.02	98	364000	115000	3.17	56	1

EO = epoxidized oil, THF:EO = monomer ratio (ml : g), Mol eq. = mol equivalent of  $\text{BF}_3.\text{Et}_2\text{O}$ , GPC = gel permeation chromatography,  $M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index, OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g)

The copolymerization reaction of THF with epoxidized oils (**2.3**) and (**2.16**) that have one epoxy group per molecule will not form cross-linked polymer even when catalyzed by 0.05 mol equivalent of  $\text{BF}_3.\text{Et}_2\text{O}$  and both the epoxidized oils (**2.3** and **2.16**) gave good yield of oligomeric polyols (97%, 93% respectively) with relatively

low PDI. The relatively high AV for **(2.3)** indicates significant hydrolysis during the reaction. While for epoxidized plant oils with multiple epoxide groups per molecule (**2.17**, **2.13**, **2.6** and **2.18**) the amount of catalyst must be less than 0.03 mol equivalents of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  to avoid formation of cross-linked products. Furthermore, the monomer ratio (THF : EO) for epoxidized oils increases with more epoxide groups per molecule as shown in Table 4.11 to avoid formation of cross-linked products. In general, epoxidized plant oils with more epoxides per molecule lead to larger molecular weights and hydroxyl values as expected.

Both **(2.18)** and **(2.17)** have 2 epoxide groups per molecule but **(2.18)** has 3 alkenes while **(2.17)** has none. Referring to Table 4.11, the copolymers made from **(2.17)** has higher  $M_n$  and OHV than copolymers made from **(2.18)**. This indicates that the alkenes of **(2.18)** has affected the properties of the copolymers and we think that the extra ‘kink’ on the fatty acid hydrocarbon chain of **(2.18)** is responsible for the lower  $M_n$  and OHV of copolymers from **(2.18)**. The epoxidized oils **(2.13)** and **(2.6)** have 4 and 5 epoxide groups per molecule respectively, which are higher than the other epoxidized plant oils in this study. This high epoxide content led to higher  $M_n$  value and hydroxyl values.

The acid values of the copolymers (1 mg KOH/g) are considered low and acceptable for use in PU formulation and this indicates little hydrolysis happened during the copolymerization reaction; however copolymers based on **(2.3)** have a higher acid value due to the relative ease of hydrolysis of the methyl ester group. The hydroxyl value of the copolymers ranges from 25 to 60 mg KOH/g sample, depending on the starting material. In general, plant oils with a higher amount of epoxide functionality

will produce a higher hydroxyl value because the hydroxyl functionality was produced from the epoxide group through epoxide ring opening reactions.

In summary, copolymers of THF and various epoxidized plant oils can be prepared through ring opening polymerization catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The properties of the copolymers depend on the degree of unsaturation of the plant oils as well as the reaction conditions (monomer ratio, catalyst amount, reaction temperature and reaction time).

These copolymers have hydroxyl groups that can react with diisocyanates, therefore they can theoretically be used to make polyurethane (PU) products. In the later sections, we will evaluate the properties of PU products made from these copolymers with PU product made from homopolymerization of THF.

#### 4.12 EFFECT OF WATER CONTENT ON THE PROPERTIES OF THE COPOLYMERS

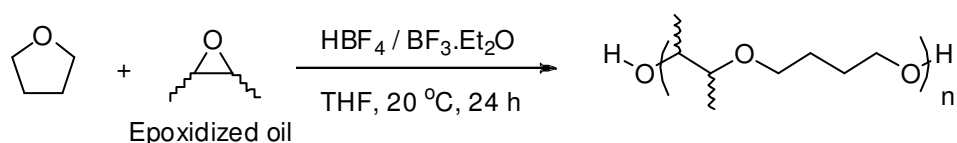


Figure 4.36 Copolymerization of THF and epoxidized oils

Earlier in Section 4.1 (page 131), the screening of chemical compounds as potential catalyst for the copolymerization reaction between THF and epoxidized plant oils was discussed. Two boron based compounds were identified as suitable catalysts for



the copolymerization reaction, they were  $\text{BF}_3\cdot\text{Et}_2\text{O}$  and  $\text{HBF}_4$ . The two boron based compounds were used to catalyze the copolymerization reaction of THF with **(2.3)** and **(2.17)** under same reaction conditions in order to evaluate the catalytic activities of both compounds (Figure 4.36). The results of this study were tabulated in Table 4.12.

Table 4.12 Properties of copolymers of THF and epoxidized oils

EO	THF:E O	Mol eq.	Catalyst	Polymer content (%)	GPC		
					$M_w$ (Da)	$M_n$ (Da)	PDI
<b>2.3</b>	5:1	0.05	$\text{BF}_3\cdot\text{Et}_2\text{O}$	87	22900	11400	2.00
<b>2.3</b>	5:1	0.05	$\text{HBF}_4$	56	3400	2700	1.26
<b>2.17</b>	30:1	0.02	$\text{BF}_3\cdot\text{Et}_2\text{O}$	97	366000	55800	6.56
<b>2.17</b>	30:1	0.02	$\text{HBF}_4$	95	85000	22500	3.78

EO = epoxidized oil, THF:EO = monomer ratio (ml : g), Mol eq. = mol equivalent of  $\text{BF}_3\cdot\text{Et}_2\text{O}$ , GPC = gel permeation chromatography,  $M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index,

Referring to Table 4.12, for both epoxidized plant oils with mono-epoxide **(2.3)** and multi-epoxides **(2.17)** group per molecule, the  $\text{BF}_3\cdot\text{Et}_2\text{O}$  catalyzed reactions yielded copolymers with larger molecular weight ( $M_n$ ) and higher polymer content. One of the main different between  $\text{BF}_3\cdot\text{Et}_2\text{O}$  and  $\text{HBF}_4$  is that  $\text{HBF}_4$  was supplied in the form of 48% in water, while  $\text{BF}_3\cdot\text{Et}_2\text{O}$  was supplied in solution of 48% in ethyl ether.

It is proposed that water content of  $\text{HBF}_4$  has significant effect on the properties of the copolymers. Therefore, the effect of water content in the reaction system on the properties of copolymers was evaluated by adding specific amount of water into the reaction system. The study was conducted with **(2.17)** as the epoxidized oil (Figure 4.37) and the results of this study were tabulated in Table 4.13.

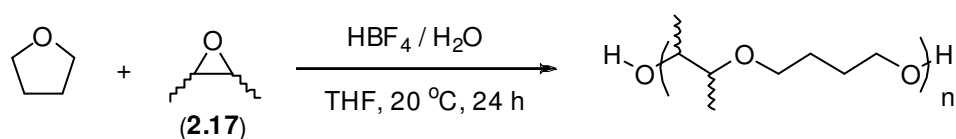


Figure 4.37 Copolymerization of (2.17) and THF with addition of water

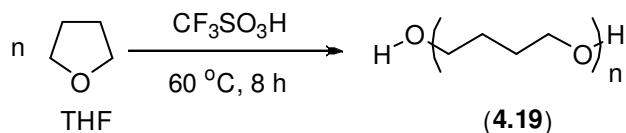
Table 4.13 Properties of copolymers from copolymerization reaction with addition of water

Entry	THF:EO	Mol eq.	Addition of water (μL)	Water content (% w/w)	Polymer content (%)	GPC		
						M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	10:1	0.02	0	0.03	Gelled	-	-	-
2	10:1	0.02	1	0.04	Gelled	-	-	-
3	10:1	0.02	5	0.08	92	81600	18700	4.36
4	10:1	0.02	10	0.13	78	12800	7900	1.62
5	10:1	0.02	100	1.06	0	-	-	-

THF:EO = monomer ratio (ml : g), Mol eq. = mol equivalent of HBF<sub>4</sub>, GPC = gel permeation chromatography, M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

The results in Table 4.13 clearly show that increasing the amount of water in the reaction system impeded the copolymerization reaction, in which at a low level of water content (Entry 1), the product was a cross-linked copolymer while at 1% water content (Entry 5), the reaction did not produce any copolymers. Comparing the data from Entry 3 and 4, the additional amount of water in Entry 4 significantly reduced the polymer content and molecular weight of copolymers. This information provides another method to control the molecular weight of the copolymer by addition of specific amounts of water into the reaction system.

### 4.13 HOMOPOLYMERIZATION OF TETRAHYDROFURAN CATALYZED BY TRIFLIC ACID



The homopolymerization of THF was conducted according to method published by Dorai<sup>105</sup> *et al.* The purpose of this work is to prepare homopolymers of THF as a benchmark in our study on the properties of PU made from copolymers of THF and epoxidized plant oils. The homopolymer of THF (**4.19**) was analyzed by GPC, MALDI-TOF-MS and <sup>1</sup>H NMR. The Table 4.14 shows the properties of (**4.19**).

Table 4.14 Properties of (**4.19**)

Mol eq.	Polymer content (%)	GPC			OHV	AV
		M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI		
0.08	100	33800	18000	1.87	40	0.5

Mol eq. = mol equivalent of CF<sub>3</sub>SO<sub>3</sub>H, GPC = gel permeation chromatography, M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index, OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g)

GPC analysis shows that the (**4.19**) has a M<sub>n</sub> = 18000 Da. While MALDI-TOF-MS analysis of (**4.19**) (Figure 4.38) shows a peak at 958 Da, which corresponds to sodium adduct of homopolymerized 13 units of THF (**4.20**) (Figure 4.39). The other peaks are (**4.20**) plus additional unit of the THF. The prepared (**4.19**) has hydroxyl functionality that can be used to make PU.

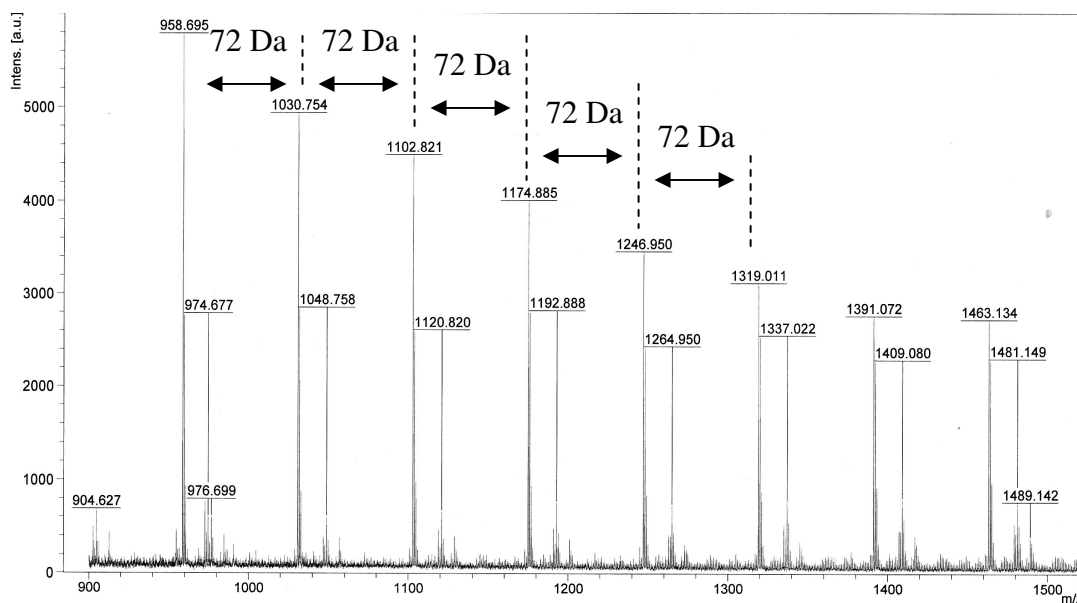


Figure 4.38 MALDI-TOF-MS spectrum of (4.19) by using DHB as matrix in the analysis

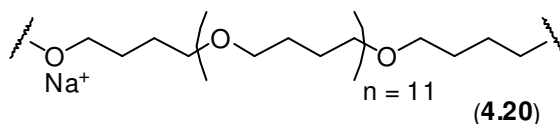


Figure 4.39 Homopolymer of THF

#### 4.14 ATTEMPTED COPOLYMERIZATION OF EPOXIDIZED PLANT OILS WITH OTHER HETEROCYCLICS

In earlier sections, the successful copolymerization of THF with epoxidized plant oils was discussed. This prompts a study to look into the possibility of copolymerizing epoxidized plant oils with other heterocyclics by using the same optimized reaction condition for copolymerization of epoxidized plant oils and THF. The first two heterocyclics that were evaluated were the analogue of THF, namely 2-methyl tetrahydrofuran (4.21) and 3-methyl tetrahydrofuran (4.22) (Figure 4.40) in order to know whether the extra methyl group at position 2 and 3 of THF ring will

affect the copolymerization reaction. The reactions were conducted with monomer ratio 20 : 1 (THF analogue : **(2.17)** ; ml : g) and with other reaction conditions as shown in Figure 4.40.

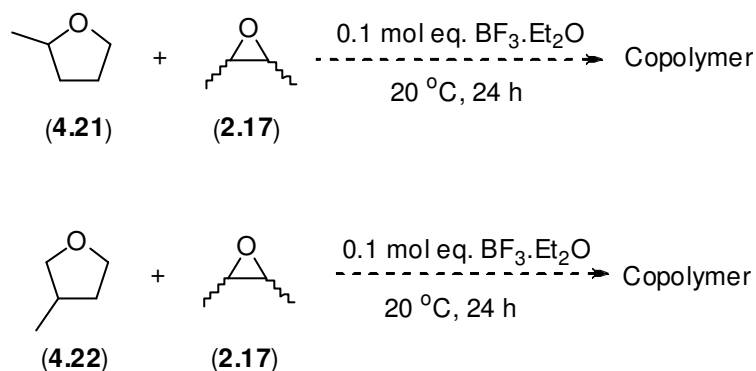


Figure 4.40 Copolymerization of **(2.17)** with **(4.21)** and **(4.22)**

After several attempts, the reactions failed to produce any copolymers of **(2.17)** and **(4.21)** or **(4.22)**. Literature<sup>106-107</sup> on homopolymerization of **(4.21)** pointed out that the **(4.21)** was not able to polymerize with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{SbCl}_5$  or  $4\text{-ClC}_6\text{H}_4\text{N}_2\text{PF}_6$  because of an unfavorable thermodynamic factor<sup>108</sup> for ring opening of **(4.21)**. Furthermore, during THF polymerization reaction, the attack of activated THF is at the  $\alpha$  position of the oxygen atom, therefore, methyl substitution at the  $\alpha$  position hinders the polymerization reaction. Chiang *et al.*<sup>109</sup> show that **(4.22)** can be polymerized using high amounts ( $>10\%$  mol) of catalysts such as  $\text{PF}_5$  and low reaction temperature ( $-22^\circ\text{C}$ ) for 45 days to yield 40% poly(3-methyltetrahydrofuran).

## 4.15 COPOLYMERIZATION OF EPOXIDIZED PLANT OILS WITH ε - CAPROLACTONE

The ε-caprolactone (**4.23**) was copolymerized with (**2.17**) using the same reaction conditions employed for the synthesis of EPO-THF (**4.10**) (Figure 4.41) to yield copolymer (**4.24**). The results of the copolymerization were tabulated in Table 4.15

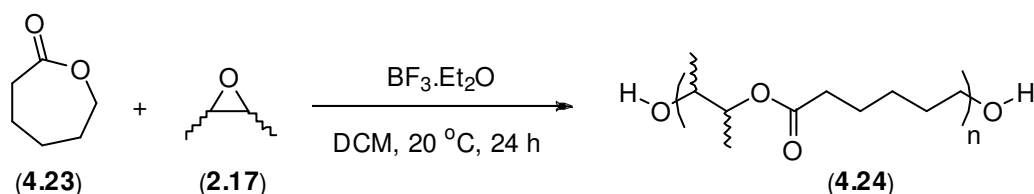


Figure 4.41 Copolymerization of (**4.23**) with (**2.17**)

Table 4.15 Properties of (**4.24**)

Entry	(4.23 : 2.17)	Mol eq.	Polymer		GPC	
			content (%)	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	0.25 : 1	0.05	77	9000	6200	1.45
2	0.5 : 1	0.05	68	7700	5600	1.37
3	1 : 1	0.05	54	6400	5400	1.18

(**4.23** : **2.17**) = monomer ratio (mol : mol), Mol eq. = mol equivalent of BF<sub>3</sub>.Et<sub>2</sub>O, GPC = gel permeation chromatography, M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index.

The result in Table 4.15 shows that the average molecular weight of (**4.24**) as well as the polymer content decreases with increasing monomer ratio of (**4.23**) to (**2.17**) in the starting mixture. This indicates that the (**4.23**) retards the oligomerization of (**2.17**).

GPC analysis shows that the average molecular weight of **(4.24)** was about 6200 Da. MALDI-TOF-MS analysis of **(4.24)** (Figure 4.42) shows a peak at 1177 Da (Figure 4.43) that correspond to structure **(4.25)**, while additional peaks are **(4.25)** plus additional units of **(4.23)**. Furthermore, oligomers of **(2.17)** plus a unit of **(4.23)** was also detected with a peak at 1953 Da, which corresponds to structure **(4.26)**.

$^1\text{H}$  NMR spectroscopy (Figure 4.44) shows that copolymers of **(4.24)** have the ring-opened  $\epsilon$ -caprolactone moiety at 4.06 ppm ( $\epsilon\text{-CH}_2$ ) and 3.61 ppm ( $\text{HO-CH}_2$ ) as well as the ether and hydroxyl moiety of copolymers at 3.58 – 3.10 ppm. Furthermore, epoxide ring opening by carboxylic group of **(4.23)** was also detected by  $^1\text{H}$  NMR at 4.84 ppm.

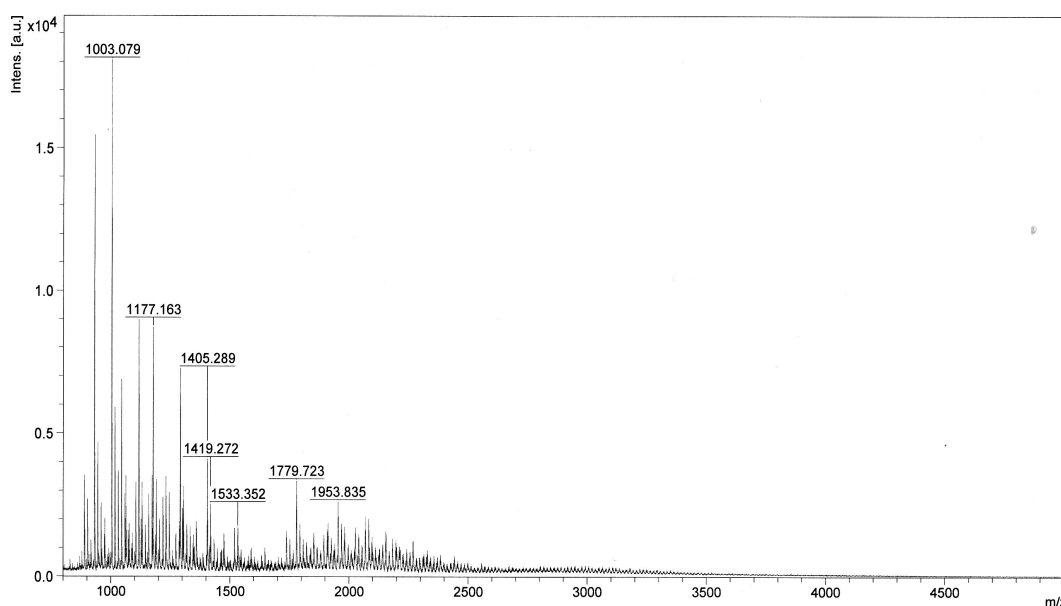


Figure 4.42 MALDI-TOF-MS spectrum of **(4.24)** by using DHB as the matrix of the analysis

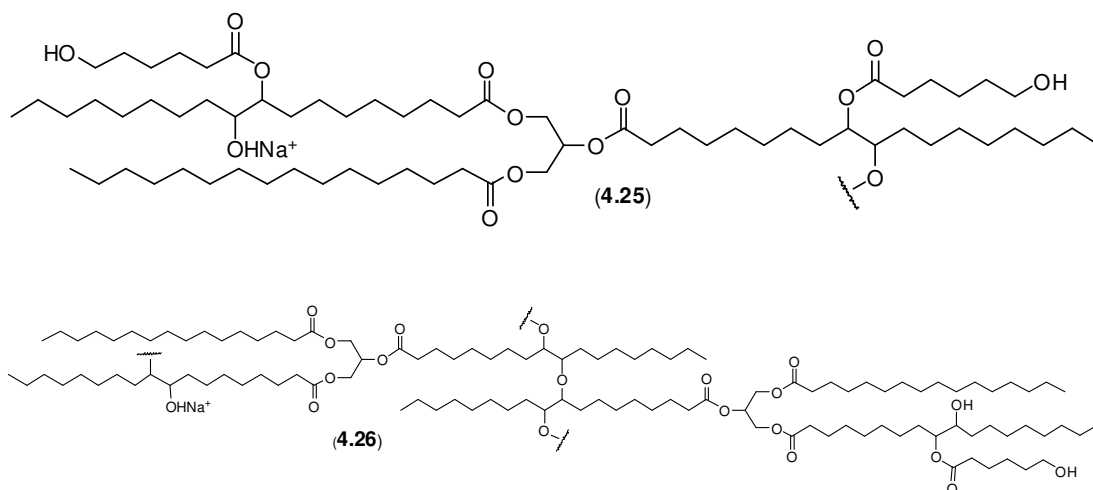


Figure 4.43 Copolymers of (4.24)

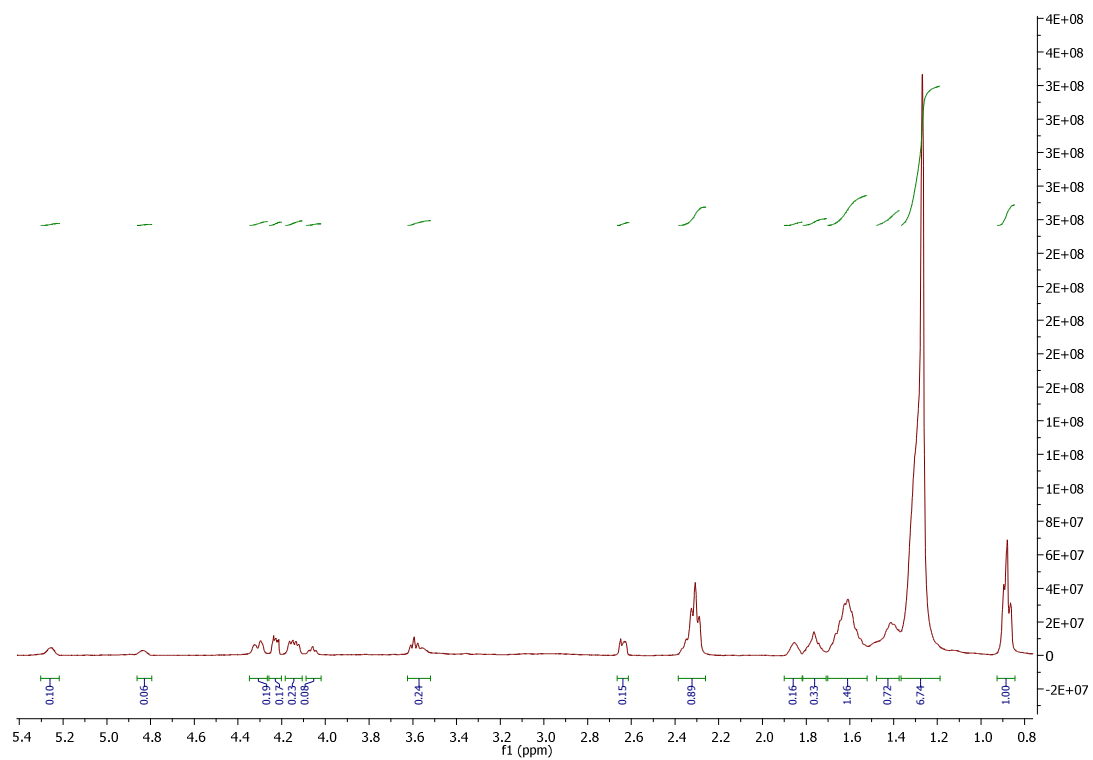


Figure 4.44 400 MHz <sup>1</sup>H NMR spectrum of (4.24) in CDCl<sub>3</sub>



#### 4.16 POLYURETHANES MADE FROM COPOLYMERS OF EPOXIDIZED PLANT OILS AND TETRAHYDROFURAN

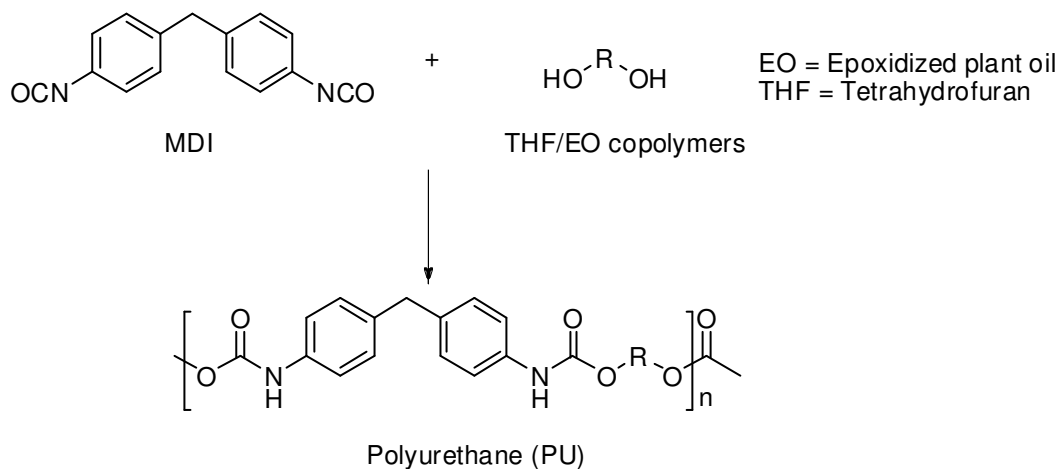


Figure 4.45 PU made from copolymers of epoxidized plant oils and THF

The prepared copolymers of epoxidized plant oils and tetrahydrofuran were used as starting materials for making polyurethane (PU) samples. These copolymers were reacted with 4,4'-diphenylmethane diisocyanate (MDI) and yielded quantitative amount of PU samples (Figure 4.45).

The ratio between the isocyanate group (NCO) and the hydroxyl group (OH) was kept at 1.05 to 1 (NCO/OH ratio = 1.05) in order to ensure that all the hydroxyl groups of copolymers were fully reacted and the PU samples were fully cured when the excess isocyanate group reacted with moisture from the air.

The PU synthesis was based on the six copolymers (**4.4**, **4.7**, **4.10**, **4.12**, **4.15** and **4.18**) and they were reacted with MDI according to ratio describe above. In addition, we have also included homopolymerized THF (**4.19**) as a control in the PU analysis. The PU samples made from these copolymers were cross-linked polymers, which

indicate that all the copolymers have 2 or more hydroxyl functionality that enable the formation of cross-linked polymer.

Tensile testing was carried out on these PU samples in order to give a better understanding of the strength of these PU. Figure 4.46 shows the stress-strain curve of PU made from each type of copolymers. Furthermore, swelling tests was conducted on the PU samples in order to determine the cross-linking density of the PU samples by using the Flory-Rehner equation.<sup>95</sup> The following Table 4.16 shows the properties of the PU samples made from these copolymers.

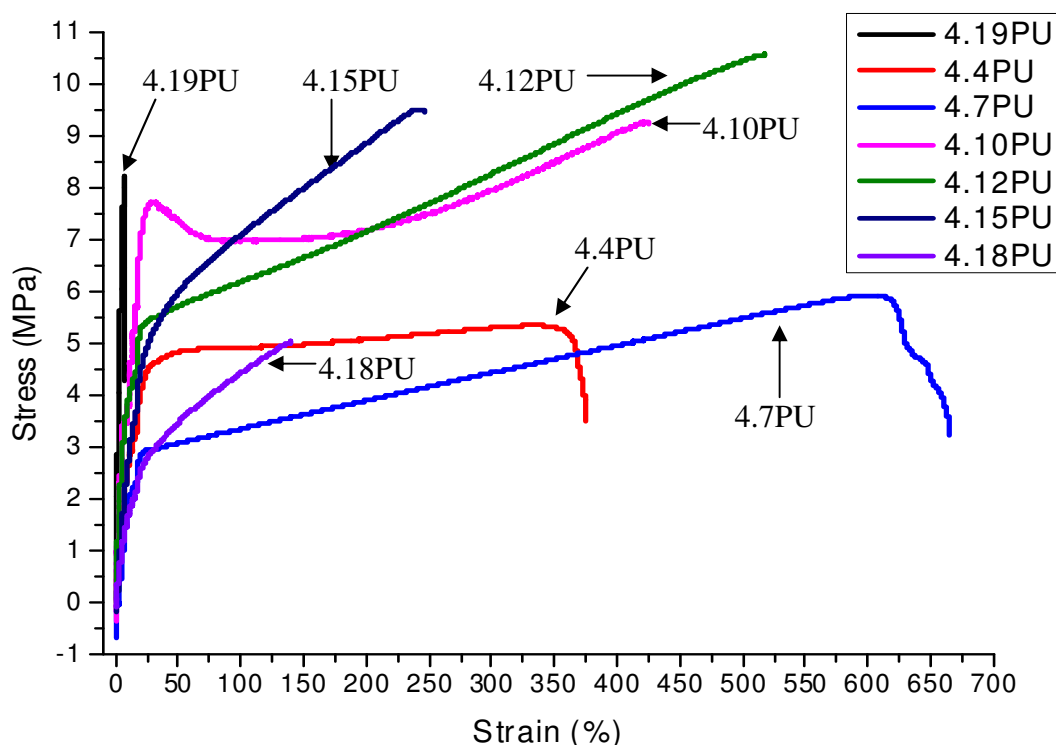


Figure 4.46 Stress-strain curves of PU samples made from copolymers according to method EN ISO 529-4: 1997(CEN1997a)

**4.19PU** – PU based on homopolymerized THF; (**4.19**)

**4.4PU** – PU based on copolymer of epoxidized methyl oleate (**2.3**) and THF; (**4.4**)

**4.7PU** – PU based on copolymer of epoxidized cocoa butter (**2.16**) and THF; (**4.7**)

**4.10PU** – PU based on copolymer of epoxidized palm oil (**2.17**) and THF; (**4.10**)

**4.12PU** – PU based on copolymer of epoxidized rapeseed oil (**2.13**) and THF; (**4.12**)

**4.15PU** – PU based on copolymer of epoxidized soybean oil (**2.6**) and THF; (**4.15**)

**4.18PU** – PU based on copolymer of euphorbia oil (**2.18**) and THF; (**4.18**)

Table 4.16 Properties of PU samples made from copolymers

PU	Tensile strength (MPa)	Elongation at break (%)	Cross-link density $\times 10^{-4}$ (mol/cm <sup>3</sup> )
4.19PU	8.3	6	0.65
4.4PU	5.3	350	3.23
4.7PU	5.9	610	3.38
4.10PU	9.1	425	5.30
4.12PU	10.5	510	6.05
4.15PU	9.5	250	7.52
4.18PU	5.0	140	3.95

Referring to Table 4.16 and Figure 4.46, the (**4.19PU**) shows significantly high tensile strength (8.3 MPa) but low elongation (6%). The tensile strength of (**4.19PU**) comes from the intermolecular force between polymer chains of (**4.19**) as the polymer chains of (**4.19**) are more regular in structure, which can form semicrystalline structure in (**4.19PU**) and this semicrystalline structure acts as a physical cross-link in the PU polymer matrix.<sup>110</sup> However, the cross-link density of (**4.19PU**) was low ( $0.65 \times 10^{-4}$  mol/cm<sup>3</sup>) because both the (**4.19**) and MDI are bifunctionals molecules that usually form linear polymers.

Both copolymers (**4.4** and **4.7**) were made from epoxidized oils with one epoxide group and the hydroxyl values of both copolymers were relatively lower than other copolymers. Therefore, the cross-link densities exhibited by PU made from both copolymers (**4.4PU** and **4.7PU**) were relatively low ( $3.2\text{-}3.4 \times 10^{-4}$  mol/cm<sup>3</sup>). This

relatively low cross-link density translated to tensile strength in the region of 5.3 MPa to 5.9 MPa. However, there is a significant difference between these two PU as the elongation at break for (**4.7PU**) was significantly higher than (**4.4PU**). This better performance of (**4.7PU**) can be attributed to the plasticizing effect from the saturated fatty acid chains found in (**4.7PU**), which originated from epoxidized cocoa butter (**2.16**).

In comparison, (**4.10PU**) made from copolymers based on epoxidized palm oil (**2.17**), which has two epoxides functionality has a higher cross-link density and tensile strength exhibited than both (**4.4PU** and **4.7PU**). However, the higher cross-link density also contributed to lower elongation at break as compared to (**4.7PU**). On the other hand, (**4.18PU**) made from (**4.18**) copolymers exhibited lower tensile strength and elongation at break as compared to (**4.10PU**) even though the copolymers (**4.18**) were made from euphorbia oil (**2.18**), which has the same level of epoxide functionalities as (**2.17**). As discussed earlier in Section 4.11 (page 156), the copolymer (**4.18**) has a lower hydroxyl value (33 mg KOH/g) as compared to (**4.10**) (40 mg KOH/g) due to the alkene groups still remaining in (**4.18**). The lower hydroxyl value of (**4.18**) contributed to lower cross-link density, tensile strength and elongation at break of (**4.18PU**). In addition, it is proposed that the extra 'kink' from alkene groups (**4.18PU**) also contributed to lower performance of (**4.18PU**) as compared to (**4.10PU**) by obstructing the packing of the PU polymer chains, which reduced the intermolecular force of the PU polymer chains.

Referring to Figure 4.46, (**4.12PU**) exhibited the highest tensile strength among all the PU samples. This is due to the relatively high cross-link density of (**4.12PU**),

which was contributed by the relatively higher hydroxyl value of **(4.12)** (48 mg KOH/g). In contrast, the **(4.15PU)** has a higher cross-link density than **(4.12PU)** due to the higher hydroxyl value of **(4.15)**. However, the elongation at break of **(4.15PU)** was lower than **(4.12PU)** even though they have similar tensile strength. It is proposed that the cross-link density of **(4.15PU)** was now too high and that it made the PU **(4.15PU)** stiffer, which restricted the elongation of **(4.15PU)**, resulting in lower elongation at break.

#### 4.17 POLYURETHANES MADE FROM COPOLYMERS OF EPOXIDIZED PLANT OILS AND $\epsilon$ - CAPROLACTONE

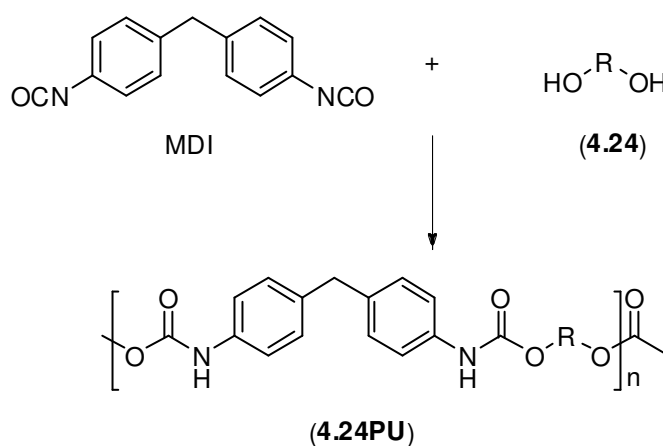


Figure 4.47 Synthesis of PU from MDI and **(4.24)**

The copolymers of **(4.24)** made from epoxidized palm oil **(2.17)** and  $\epsilon$ -caprolactone **(4.23)** were reacted with MDI (Figure 4.47) according to reaction condition described in Section 4.16 to produce **(4.24PU)**. The **(4.24PU)** was subjected to tensile strength evaluation as well as swelling test in order to evaluate the physical properties of the PU. The following Figure 4.48 shows the stress-strain curve of **(4.24PU)**.

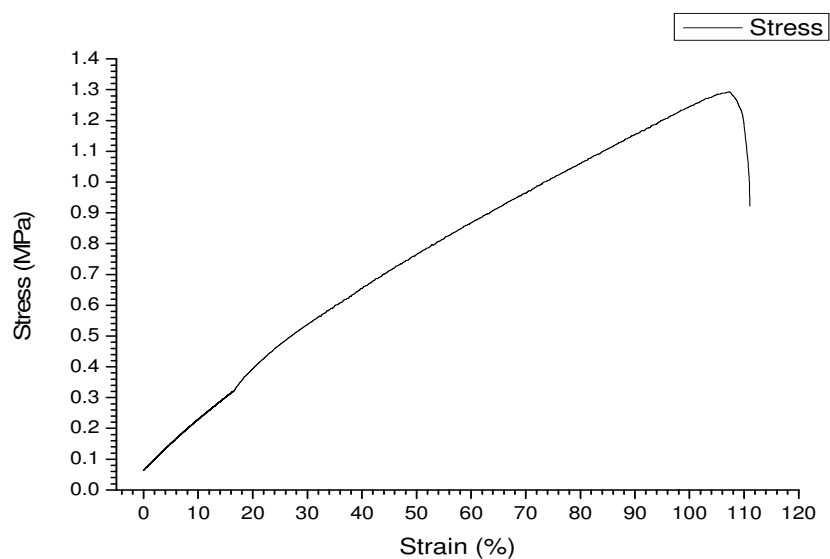


Figure 4.48 Stress-strain curve of **(4.24PU)** according to method EN ISO 529-4: 1997(CEN1997a)

Figure 4.48 show that **(4.24PU)** has relatively low tensile strength and elongation at break. This may be due to the relatively low average molecular weight of **(4.24)**, which range from 5000 Da to 6000 Da as compared to THF based copolymers which range from 26000 Da to 110000 Da. The properties of cross-linked PU, such as tensile strength and elongation generally increase with the increasing molecular weight of the polyols.<sup>101</sup>

#### 4.18 THERMAL PROPERTIES OF POLYURETHANES MADE FROM COPOLYMERS

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted on the prepared PU samples made from copolymers in order to evaluate the thermal properties of these PU samples. In addition, PU made from

homopolymerized THF (**4.19**) was also evaluated for comparison purposes. The following are the results of the thermal analysis.

### Thermal gravimetric analysis (TGA)

The following Figure 4.49 and 4.50 show the TGA analysis of PU samples made from copolymers and (**4.19**).

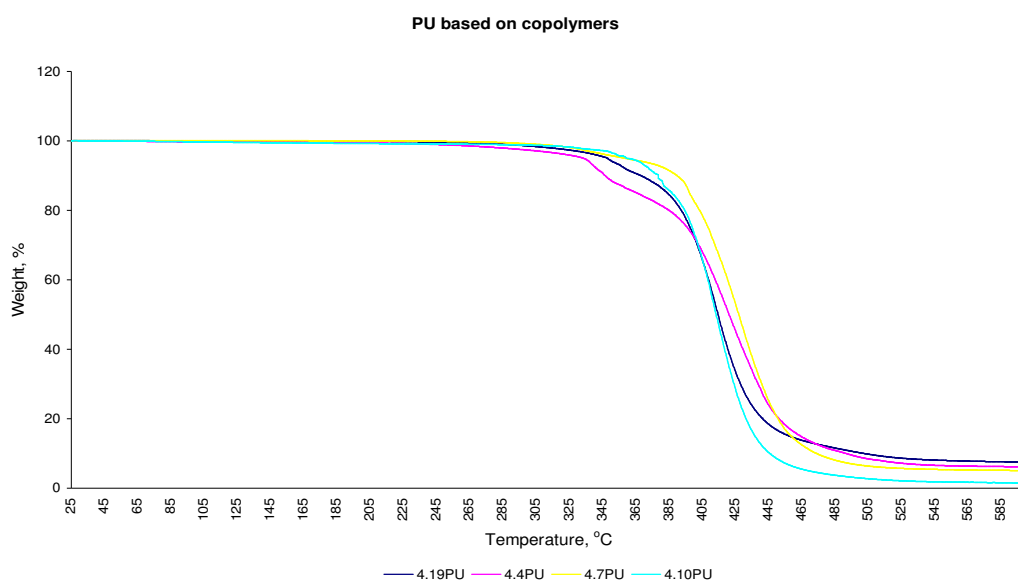


Figure 4.49 TGA analysis of PU samples (**4.4PU**, **4.7PU** and **4.10PU**) and (**4.19**)

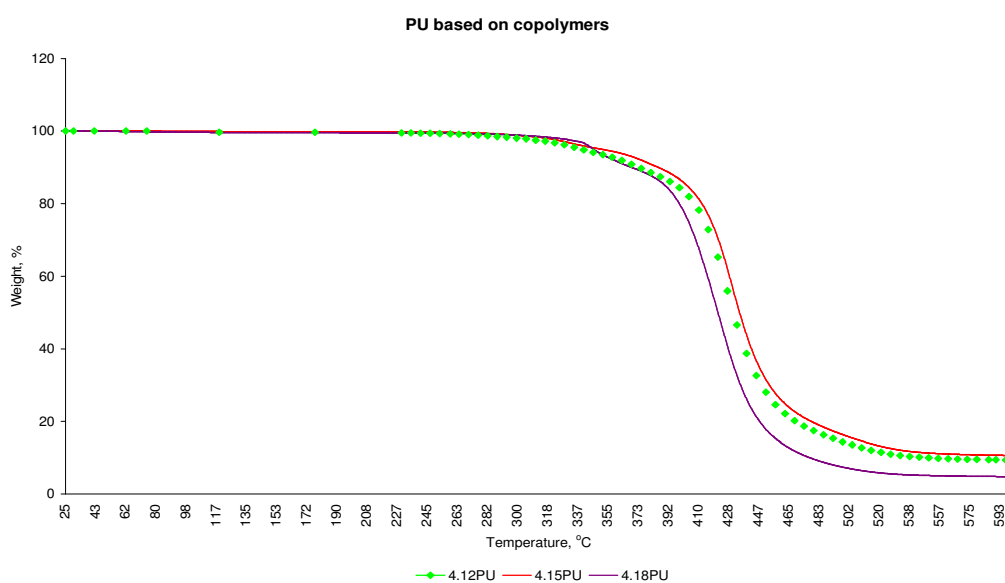


Figure 4.50 TGA analysis of PU samples (**4.12PU**, **4.15PU** and **4.18PU**)

Referring to Figure 4.49 and 4.50, the PU made from copolymers and homopolymers of THF started to degrade at about 300 °C. The TGA analysis also shows that some of the PU samples (**4.4PU** and **4.18PU**) exhibit a minor component and a major component in the samples. The minor component could be unreacted fatty acids / triglycerides. Meanwhile, the evaluated PU samples (**4.7PU**, **4.10PU**, **4.12PU** and **4.15PU**) exhibit one component in the samples. All the PU samples were thermally stable up to 300 °C before they all start degrading.

### Differential Scanning Calorimetry (DSC)

The following Figure 4.51 and 4.52 show the DSC analysis of PU samples made from the copolymers. The DSC analysis shows that all the PU made from the copolymers have glass transition temperatures ( $T_g$ ) at about -70 °C. This low  $T_g$  contributed to the flexibility of the PU and they are able to remain flexible even at low temperatures. Furthermore, each of the PU samples exhibited a softening/melting point at temperature ranges from 10 °C to 45 °C, depending on the copolymers used in making the PU before they degraded at 300 °C.

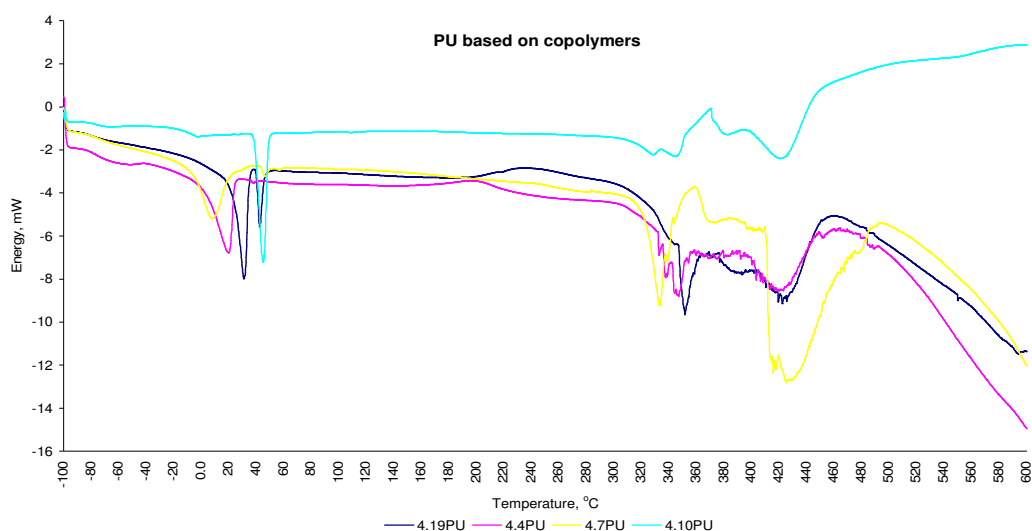


Figure 4.51 DSC analysis of PU samples (**4.19PU**, **4.4PU**, **4.7PU** and **4.10PU**)



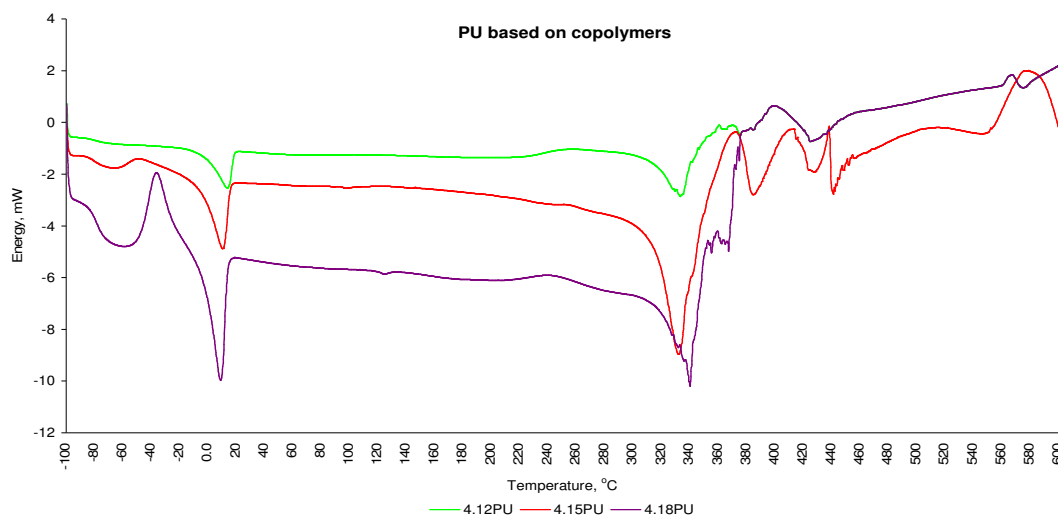


Figure 4.52 DSC analysis of PU samples (**4.12PU**, **4.15PU** and **4.18PU**)

#### 4.19 SUMMARY

The prepared epoxidized plant oils (**2.3**, **2.16**, **2.17**, **2.13**, **2.6** and **2.18**) can be copolymerized with THF to yield copolymers polyols through cationic ring opening reaction of both epoxide and THF catalyzed by  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The copolymerization reaction was affected by the amount of catalyst, reaction temperature, reaction duration and the ratio between the two monomers (epoxidized plant oils and THF).

The properties of the copolymers also depended on the degree of unsaturation of the plant oils. Plant oils with low unsaturation [methyl oleate (**2.8**), cocoa butter (**2.9**)] will yield copolymers with lower molecular weights (**4.4** and **4.7**); while plant oils with two or more unsaturations will produce high molecular weight copolymers and higher hydroxyl values (**4.10**, **4.12**, **4.15** and **4.18**).

The prepared copolymers were used to make PU samples. PU based on copolymers made from plant oil with low levels of unsaturation (**2.3**, **2.16**) formed PU samples (**4.4PU** and **4.7PU**) with lower levels of tensile strength but with acceptable elongation (flexibility). In fact, (**4.7PU**) showed the highest elongation at break due to the plasticizing effect from the saturated fatty acid chains found in (**4.7PU**). These PU samples (**4.4PU** and **4.7PU**) have suitable mechanical properties for making elastomeric PU that requires very good flexibility. On the other hand, PU samples based on copolymers made from plant oils with higher levels of unsaturation (**4.10PU**, **4.12PU** and **4.15PU**) exhibited higher tensile strength and elongation. The highest tensile strength was exhibited by (**4.12PU**). These PU samples have suitable mechanical properties for making semi-flexible PU elastomers that require high tensile strength with some flexibility.

Thermal gravimetric analysis (TGA) shows that most the PU samples made from copolymers were stable up to 300 °C. The TGA analysis also shows that PU samples (**4.4PU** and **4.18PU**) exhibit a minor component and a major component in the samples. The minor component could be unreacted fatty acids/triglycerides. Meanwhile, PU samples (**4.7PU**, **4.10PU**, **4.12PU** and **4.15PU**) exhibit one component in the samples. The DSC analyses also reveal that all the PU samples have melting/softening points between 10 °C to 45 °C, depending on the copolymers used in making the PU sample. The DSC analysis also shows that all the PU samples have glass transition temperatures at about -70 °C, which is relatively low and this makes them suitable for applications that require low temperature flexibility.

## CHAPTER 5 – ONE-POT OLIGOMERIZATION OF PLANT OIL DERIVATIVES

### 5.0 INTRODUCTION

On a commercial scale, the epoxidation of unsaturated plant oil (**5.1**) is carried out through the Prileshajev reaction, in which a peroxy acid is the epoxidation agent generated from a short-chain organic acid such as formic acid<sup>111</sup> (Figure 5.1). However, the selectivity of this reaction seldomly exceeds 90% due to side reactions such as dimerization of epoxidized plant oil (**5.2**) through ring opening of epoxide group by hydroxylated plant oil (**5.3**) generated *in-situ* during the reaction (Figure 5.2). The amount of dimerized plant oil (**5.4**) found in the reaction products was about 2% as analyzed by the GPC method.<sup>111</sup> In addition, analysis results reported in Chapter 2 (page 60) show that during the epoxidation of (**5.1**) with a tungsten based catalyst system, the reaction produced about 4% of (**5.4**) as a side product. In general, the amount of oligomers generated as side products during epoxidation of (**5.1**) was about 2% to 4%.

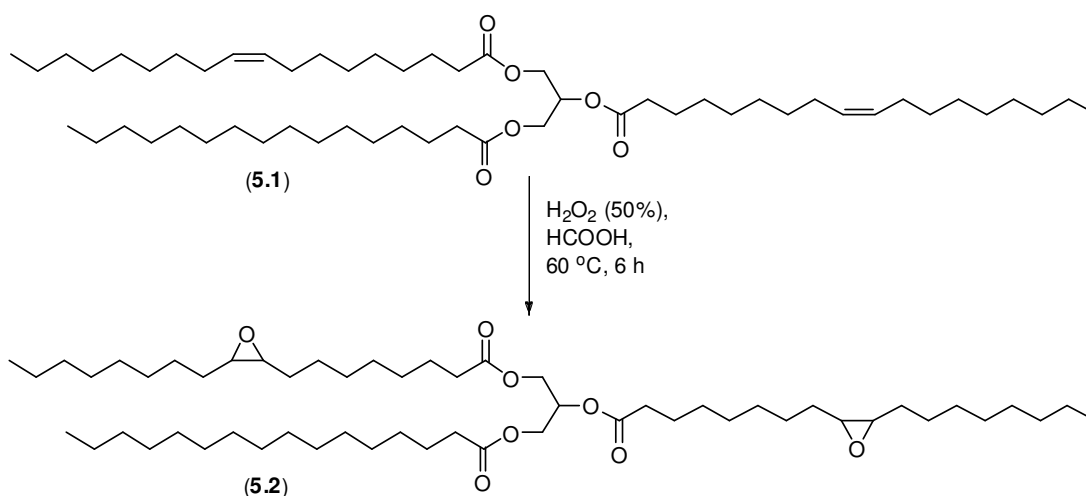


Figure 5.1 Epoxidation of palm oil with formic acid and hydrogen peroxide

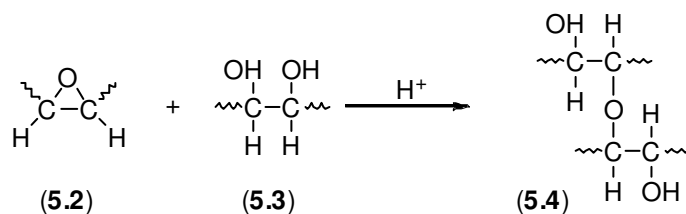


Figure 5.2 Dimerization of epoxidized plant oil

In comparison, more significant amount of oligomeric products were obtained during the ring-opening of epoxidized soybean oil (**2.6**) with water<sup>85</sup> catalyzed by phosphoric acid. Likewise, the ring-opening of epoxidized soybean oil in methanol<sup>86</sup> catalyzed by fluoroboric acid was also reported to produce about 20% oligomers of triglycerides. In addition, results in Chapter 2 (page 94) show that oligomeric plant oils can be produced from homopolymerization of epoxidized plant oils in good yield. However, this process requires two steps namely epoxidation followed by epoxide ring opening. This prompted a study to investigate the possibility of producing oligomeric plant oils using a one-pot method.

## 5.1 DIRECT OLIGOMERIZATION OF PLANT OIL WITH TUNGSTEN BASED CATALYST

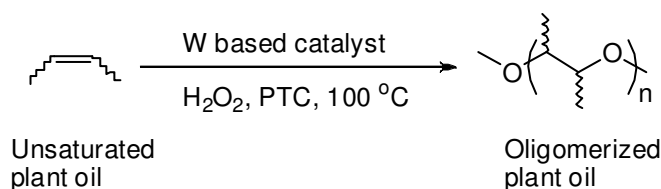


Figure 5.3 Oligomerization of unsaturated plant oils

Having established that low oligomerization (2-4%) can occur during the epoxidation reaction of rapeseed oil catalyzed by tungsten powder as described in Chapter 2

(page 60), the next step was to investigate how the amount of oligomers can be increased by a) changing the catalyst ( $\text{Na}_2\text{WO}_4$ ) and b) changing the plant oils feedstock (rape, palm, soy etc). The effect of these changes was compared at 100 °C (Figure 5.3). The experimental conditions for this study were listed in Table 5.1 and the results of this study were tabulated in Table 5.2.

Table 5.1 Experiments conducted with various plant oils and reaction conditions

Entry	Plant oil	Catalyst	Mol equivalent
1	Palm	$\text{Na}_2\text{WO}_4$	100: 2: 2: 500: 0: 0
2	Soy	$\text{Na}_2\text{WO}_4$	100: 2: 2: 500: 0: 0
3	50%Palm + 50% Soy	$\text{Na}_2\text{WO}_4$	100: 2: 2: 500: 0: 0
4	Rapeseed	$\text{Na}_2\text{WO}_4$	100: 2: 2: 500: 0: 0
5	Rapeseed	$\text{Na}_2\text{WO}_4$	100: 2: 2: 150: 0: 0
6	50%Palm + 50% Soy	W powder	100: 0.5: 0.3: 95: 65: 1450
7	Rapeseed	W powder	100: 0.5: 0.3: 95: 65: 1450

Mol equivalent = (alkene:catalyst:PTC: $\text{H}_2\text{O}_2$ :Acid: $\text{H}_2\text{O}$ ), PTC= phase transfer catalyst Adogen 464; Acid=  $\text{H}_3\text{PO}_4$

Table 5.2 Analysis results of reaction products

Entry	Gel permeation chromatography (GPC)				Yield %
	Oligomer (%)	$M_w$ (Da)	$M_n$ (Da)	PDI	
1	20	2800	2600	1.08	85
2	24	3100	2700	1.15	88
3	33	3300	2800	1.18	85
4	27	2900	2600	1.12	84
5	18	5600	4900	1.20	83
6	23	3600	3100	1.16	83
7	39	11300	6700	1.67	81

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index

Referring to Table 5.2, direct oligomerization of palm oil (Entry 1) with  $\text{Na}_2\text{WO}_4$  yielded 19.5% oligomers and GPC analysis showed that the oligomers have a  $M_n$  of about 2600 Da, which indicates the formation of mainly dimers. The low amount of oligomers could be attributed to the relatively low unsaturation in palm oil. The  $^1\text{H}$  NMR spectrum of the product shows a significant peak at 3.2 -2.8 ppm, which indicates unreacted epoxide groups. When plant oils with higher alkene contents were used as the starting material, namely soya bean oil (Exp. 2), the amount of oligomers formed (24%) in the reaction product was higher than palm oil (19%) while the  $^1\text{H}$  NMR analysis shows the complete disappearance of the epoxide moiety, which suggests more effective formation of oligomers due to the higher amount of alkene group in the starting material.

#### Mixture of palm and soy oil

When an equal mixture of palm and soy oil was used (Exp. 3) as starting material, the amount of oligomers formed in the product was measured at 32.8%. This is significantly higher than observed in experiments conducted with pure soy (Exp.2) or pure palm oil (Exp.1). This suggests that the combination of soy and palm oil enhances the formation of oligomers in some way and may be due to the almost equal amount of oleic and linoleic acid found in the 50:50 mixtures of soy and palm oil.

In general the highest level of oligomers was formed using our original tungsten powder procedure (Entry 7, 39%) but this was not high enough to be useful as a one pot oligomerization procedure.

## 5.2 OLIGOMERIZATION OF OLEIC ACID

Due to the complexity of the triglyceride mixtures, similar reactions were conducted on simple fatty acids as model compounds (Figure 5.4). Oleic acid (**5.5**) (a monounsaturated fatty acid) was subjected to the oligomerization reaction with  $\text{Na}_2\text{WO}_4$  as the catalyst and Adogen 464 as the phase transfer catalyst (PTC). These experiments were conducted with  $\text{Na}_2\text{WO}_4$  as opposed to W powder because of a simpler experiment procedure. The gel permeation chromatography (GPC) analysis shows that 75% of the crude product from the reaction consists of dimer and higher oligomers. A detailed analysis is shown below (Table 5.3).

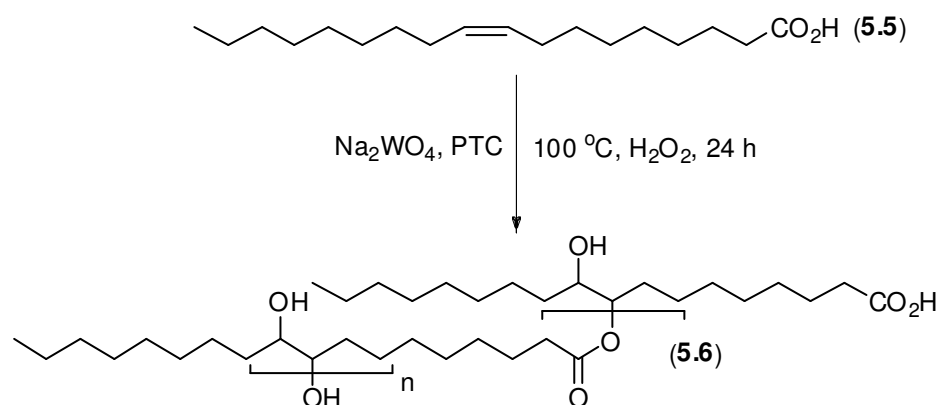


Figure 5.4 Oligomerization of (**5.5**) with  $\text{Na}_2\text{WO}_4$  and  $\text{H}_2\text{O}_2$

Table 5.3 GPC analysis of crude product from oligomerization of oleic acid

Component detected	Gel permeation chromatography (GPC)			Content %
	$M_w$ (Da)	$M_n$ (Da)	PDI	
1	2800	2500	1.12	38
2	1400	1400	1.00	24
3	890	870	1.02	27
4	530	520	1.02	11

$M_w$  = weight average molecular weight,  $M_n$  = number average molecular weight, PDI = polydispersity index





Compound **(5.6)** was analyzed with MALDI-TOF-MS that usually detects protonated molecular ions  $[M+H]^+$  and also sodium adduct ions  $[M+Na]^+$  as well as fragmentation ions. The MALDI-TOF-MS analysis of **(5.6)** shows molecular weight ranges from 500 Da to 2000 Da with the dominant mass peak at 1104 Da (Figure 5.7). This 1104 Da mass peak corresponds to the cleaved sodium adducts  $[M+Na]^+$  **(5.7)** of tetramer ( $n=4$ )( $M=1233$  Da) as shown in Figure 5.8. Furthermore, the dimer, trimer and pentamer sodium ion adduct were also detected in the mass spectra of **(5.6)** at 637 Da, 935 Da and 1531 Da respectively. This further confirms that the reaction produced oligomers of oleic acid linked by the ester group (estolides) and the major product was the tetramer of oleic acid.

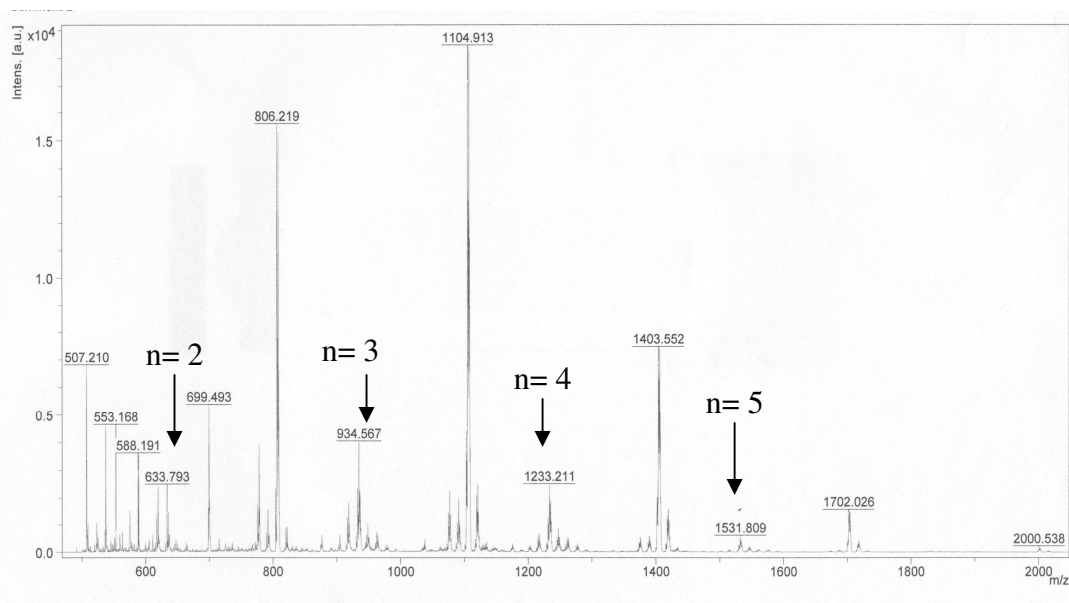


Figure 5.7 MALDI-TOF-MS spectrum of **(5.6)** by using DHB as the matrix in the analysis

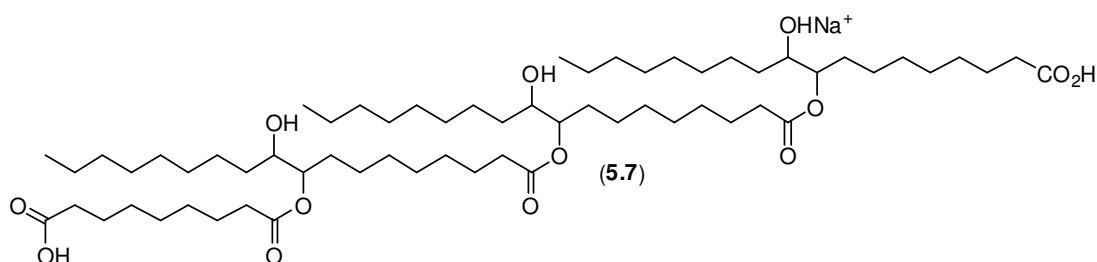


Figure 5.8 Cleaved sodium adduct of **(5.6)**

These results show that the oleic acid was oligomerized to form estolides with the proposed chemical structure (5.6). The formation of estolides from oleic acid through this one-pot oligomerization reaction is believed to occur *via* a two steps process. The first step is believed to be the conversion of the alkene (C=C) group to the epoxide group through  $\text{Na}_2\text{WO}_4$  catalyzed epoxidation reaction with hydrogen peroxide and the second step involves ring opening of the newly formed epoxy group by the carboxylic acid group of another fatty acid to yield the observed estolides (Figure 5.9). Based on MALDI-TOF-MS mass spectrum, the most abundant oligomer is the tetramer of oleic acid, followed by trimer and dimer.

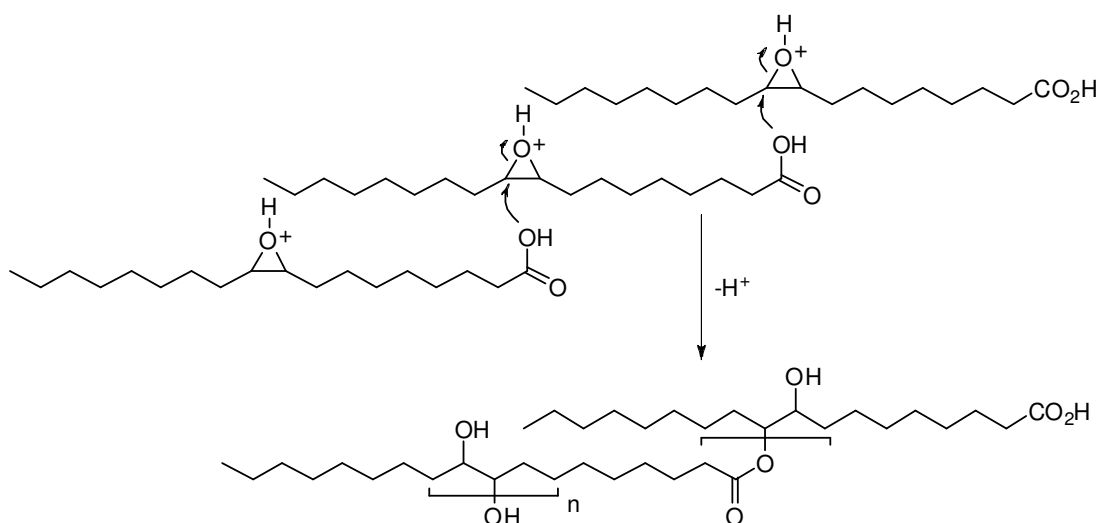


Figure 5.9 Proposed mechanism for epoxy ring opening by carboxylic acid group of another fatty acid to yield the estolides

When the same reaction was conducted with methyl oleate (5.8) (in substitution of oleic acid) (Figure 5.10), no formation of oligomers was observed. The  $^1\text{H}$  NMR spectrum of the crude product (Figure 5.11) from this reaction shows a singlet at  $\delta = 3.55$  ppm, which corresponds to the methyl of ester group and supports the idea that oligomerization did not take place.

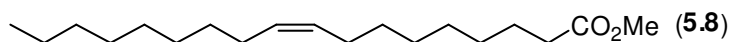


Figure 5.10 Chemical structure of methyl oleate (5.8)

Furthermore, no significant peaks at  $\delta = 3.7$  ppm and 4.85 ppm were observed, which correspond to methine proton attached to carbon atom of a hydroxyl group (HO-C-H) and an ester group (O=C-O-C-H) at 3.7 ppm and 4.85 ppm respectively as seen in Figure 5.5. Again, this indicates no formation of oligomerized oleate compounds (estolides). The product from this reaction is dihydroxy methyl stearate (5.9) (Figure 5.12), which shows a peak at  $\delta = 3.33$  ppm in  $^1\text{H}$  NMR spectrum that corresponds to the methine proton attached to carbon atom of a hydroxyl group (HO-C-H) (Figure 5.11).

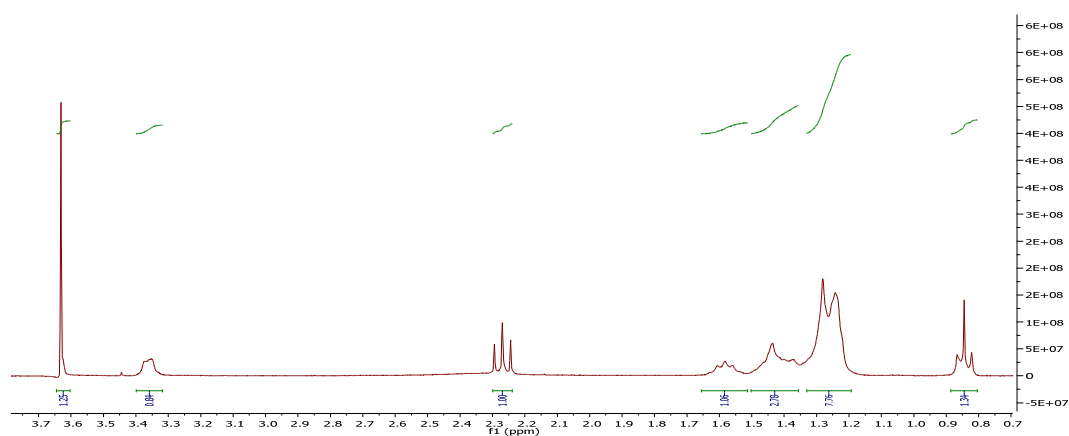


Figure 5.11 400 MHz  $^1\text{H}$  NMR spectrum of (5.9) in  $\text{CDCl}_3$

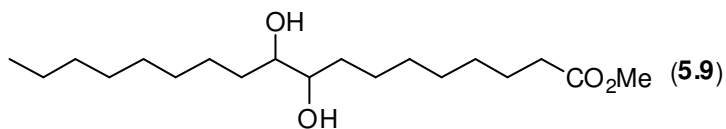


Figure 5.12 Dihydroxylated methyl oleate (5.9)

The other chemical compound that could be produced from the oligomerization reaction of oleic acid is a polyether polyol (5.10) where an alcohol has reacted with

an epoxide instead of a carboxylic acid. This alternative product will have the same mass ion as discussed above for (5.6). The possible chemical structure is illustrated in Figure 5.13, which is an oligomer of oleic acid linked by ether functionality.

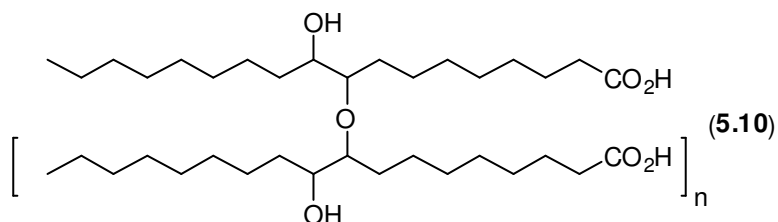


Figure 5.13 Oligomers of oleic acid linked by ether functionality

This oligomer could be produced when the oxirane group of epoxidized oleic acid was ring opened by water to yield initially a dihydroxyl group (HO-C-C-OH) and then one of the newly formed hydroxyl groups can attack the epoxide group of another epoxidized oleic acid molecule to form an ether linkage between the two fatty acid chains (Figure 5.14). The other hydroxyl group could repeat this process and form higher oligomers.

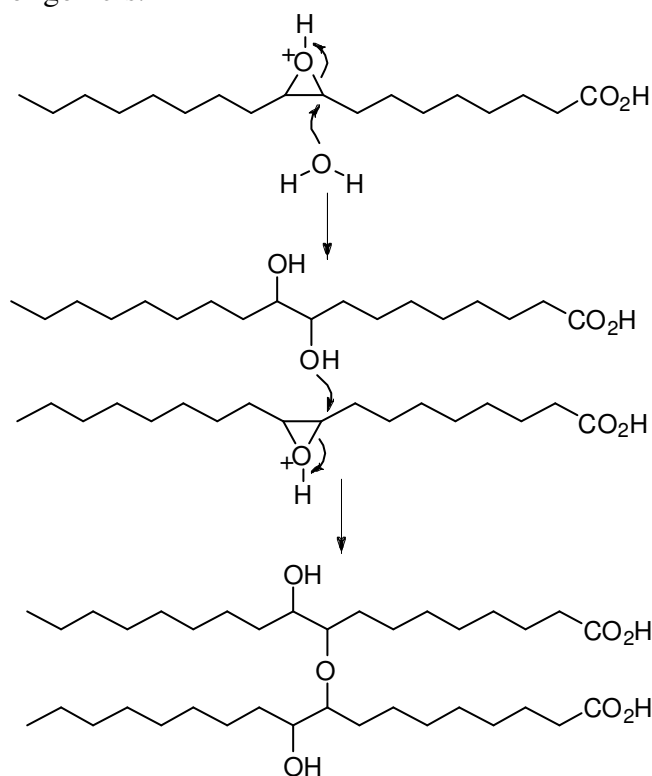


Figure 5.14 Mechanism for the formation of oleic acid oligomers linked by ether group

### Reduction and saponification of (5.6)

In order to further confirm the chemical structure of (5.6) and rule out the formation of (5.10), the oligomerized compound (5.6) was subjected to two reactions, namely reduction ( $\text{LiAlH}_4$ ) and saponification ( $\text{NaOH}$ ).  $\text{LiAlH}_4$  is a strong reducing agent and it is capable of reducing ester bonds to alcohols. Therefore, when oligomerized product (5.6) was subjected to reduction with  $\text{LiAlH}_4$ , the ester linkages between the repeating units of oleic acid should be broken and reduced to alcohol groups (causing depolymerization). If however the linkages between the monomers were ether linked then the compound would not be reduced to monomer. The same concept applies to the saponification reaction, where the ester linkages between monomer will be cleaved by  $\text{NaOH}$  but will not be cleaved if the linkages between monomer were ether groups.

When (5.6) was subjected to saponification and the crude product was purified by column chromatography the major product produced from the reaction was 9,10-dihydroxystearic acid (5.11). Reduction reaction of oligomerized product (5.6) with  $\text{LiAlH}_4$  gave 1,9,10-trihydroxysterol (5.12) as the major product (Figure 5.15). Both these reactions indicate that the linkage between fatty acid units was the expected ester linkage and ruled out an ether linkage.

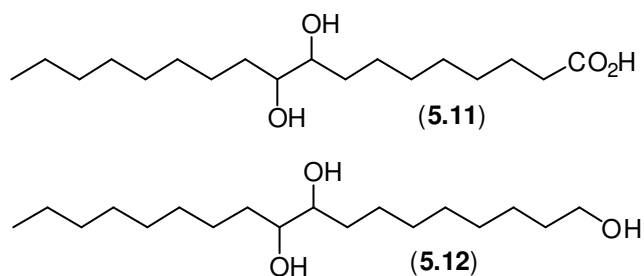


Figure 5.15 Major products from saponification and reduction of (5.6)

### Minor component from saponification reaction

While the major product isolated from the saponification reaction of (5.6) was 9,10-dihydroxy stearic acid (5.11), a minor component was also isolated from the column and identified as the alternative polyether polyol (5.13) (10% yield), in which the repeating units of oleic acid were linked by an ether group. ESI mass spectrometry of this polyether polyol shows a dominant peak at 637  $[M+Na]^+$ , which correspond to a dimer of (5.11) linked by an ether bond with molecular structure (5.13) as depicted in Figure 5.16.

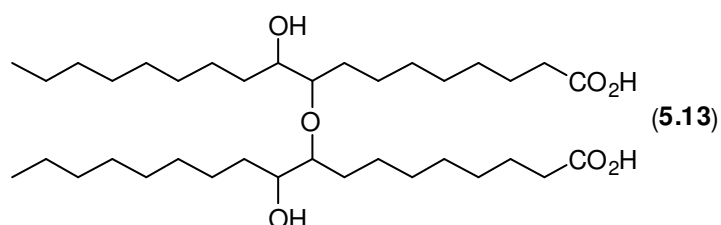


Figure 5.16 Oleic acid oligomers linked by ether group

In conclusion, analysis of the product arising from  $Na_2WO_4$  reaction with oleic acid suggests a composition of 90 % ester linked (5.6) and 10 % ether linkage (5.13).

### 5.3 1,9-NONANEDIOIC (AZELAIC ACID)

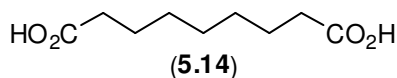


Figure 5.17 Azelaic acid

During the oligomerization of oleic acid, a co-product was isolated namely 1,9-nonanedioic (5.14) (azelaic acid) (Figure 5.17). Azelaic acid dissolves in hot water; therefore it dissolved in the aqueous layer during the oligomerization reaction but crashed out from the cooled aqueous layer as a white solid during product work-up at room temperature. The yield of azelaic acid obtained in this way from the

oligomerization reaction was low (about 2%), however, due to its known applications in polymer (nylon 69) and anti-acne products, the renewable nature of this co-product made it a target of further study. In particular, how is the azelaic acid formed during the oligomerization of oleic acid and is it possible to maximize the yield of this co-product?

The azelaic acid could be produced from oxidative cleavage of one or more compounds involved in the oligomerization reaction, namely the starting material (oleic acid) (**5.5**), the intermediate product epoxidized oleic acid (**5.15**) or product [dihydroxystearic acid (**5.11**), ester linked (**5.6**) and ether linked (**5.13**) oligomers] (Figure 5.18). Therefore by subjecting these compounds individually to the same oligomerization reaction conditions, the intermediate responsible for the formation of (**5.14**) can be determined.

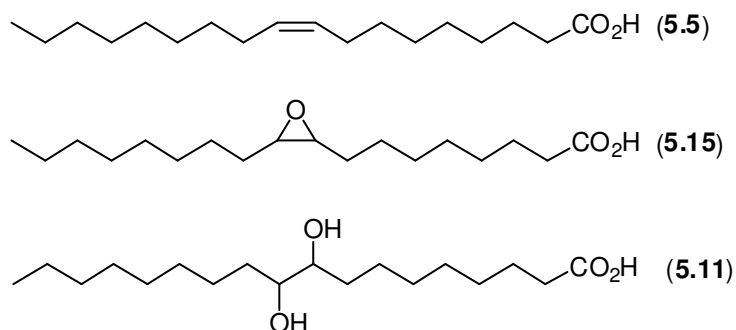


Figure 5.18 Chemical compounds involved in the oligomerization reaction

In order to achieve this goal, some oleic acid model derivatives were synthesized that represented the potential intermediate compounds involved in the oligomerization reaction. The oleic acid derivatives (**5.11**, **5.16**, **5.17**, **5.18**) (Figure 5.19) were synthesized and subjected to the oligomerization reaction conditions.

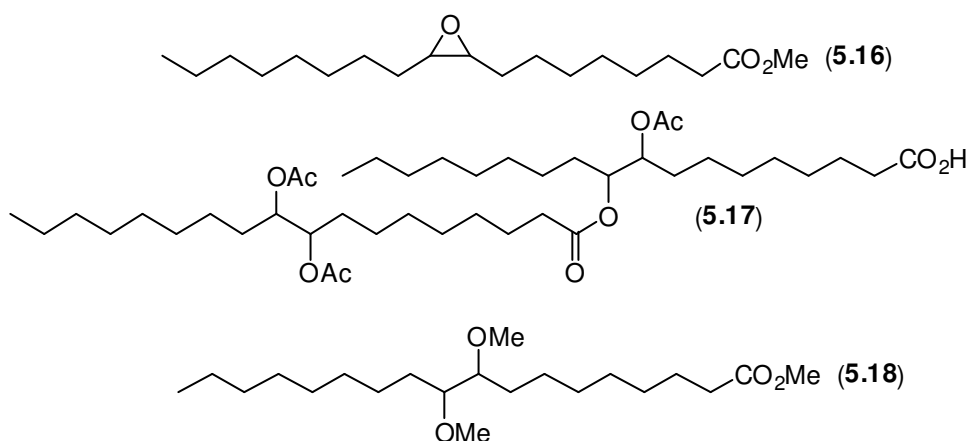


Figure 5.19 Synthesized oleic acid model derivatives

The following Figure 5.20 – 5.23 shows the synthesis of these oleic acid derivatives. Compound **(5.16)** represents an intermediate in the oligomerization of oleic acid while compounds **(5.11)**, **(5.17)** and **(5.18)** represent models of possible products from the oligomerization reaction of oleic acid. Compound **(5.11)** is the monomer of the oligomers while both **(5.17)** and **(5.18)** represent possible oligomers from the reaction. Compound **(5.17)** has a similar estolide carbon backbone structure to **(5.6)** with the addition of three acetyl groups to mimic further the oligomers of oleic acid linked by ester linkages (estolides oligomers). Meanwhile, the compound **(5.18)** has two methoxy groups that mimic the oligomers of oleic acid linked by ether linkages (polyether oligomers).

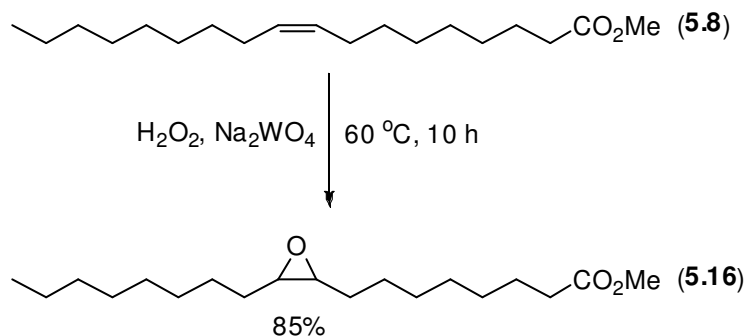


Figure 5.20 Synthesis of epoxidized methyl oleate **(5.16)**



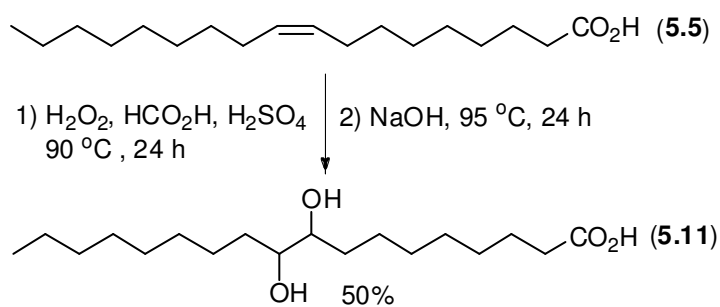


Figure 5.21 Synthesis of 9,10-dihydroxystearic acid (**5.11**)

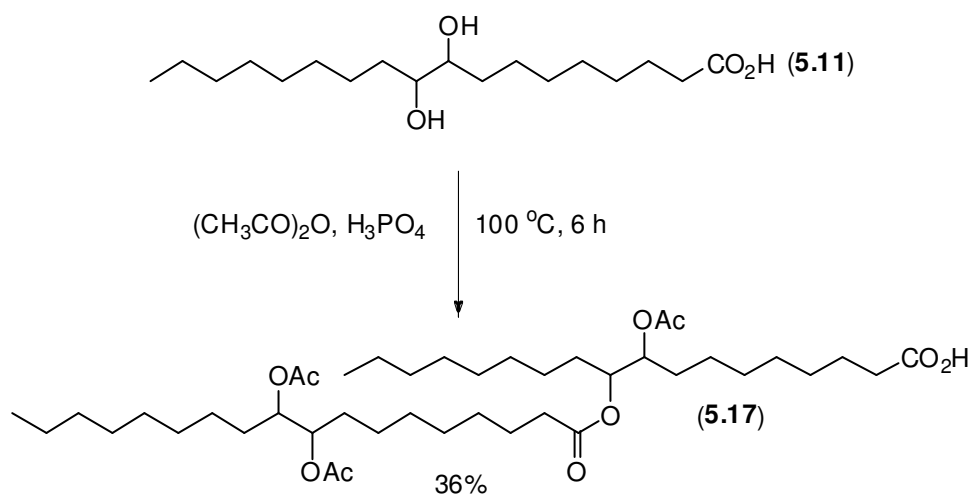


Figure 5.22 Synthesis of triacetyl estolides (**5.17**)

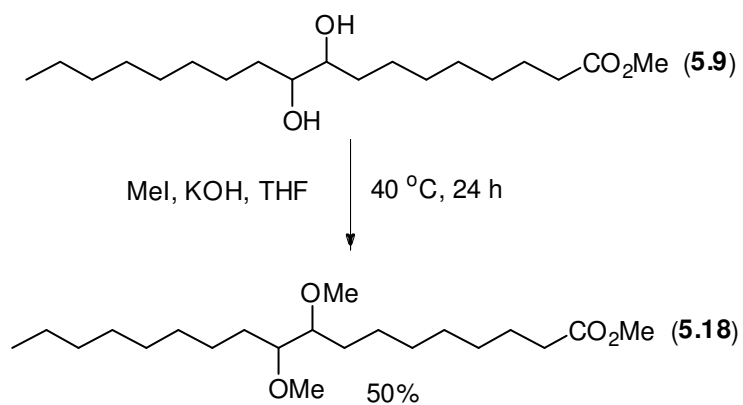


Figure 5.23 Synthesis of 9,10-dimethoxystearic methyl ester (**5.18**)

Each of the four potential precursors to azelaic acid were reacted under the original oligomerization reaction conditions (namely 5 molar equivalents of  $\text{H}_2\text{O}_2$  at 100 °C for 8 hours, catalyzed by  $\text{Na}_2\text{WO}_4$  and a phase transfer catalyst, Aliquat 336).

Based on analysis results, the formation of azelaic acid could only be detected when (5.11) and (5.16) were subjected to the oligomerization reaction with 1% and 3% yields respectively. Both (5.17) and (5.18) did not yield any azelaic acid when subjected to the same reaction conditions. Therefore, this indicates that the oxidative cleavage is a side reaction that happens before the formation of oligomers and it is not a continuation from the oligomerization reaction.

#### **5.4 OPTIMIZATION OF OLEIC ACID OLIGOMERIZATION TO ESTOLIDE (5.6)**

##### Effect of reaction temperature

This study was conducted to determine the most appropriate temperature for the oligomerization reaction. The temperature of the reaction was varied from 60 °C to 100 °C, while the other reaction parameters were kept constant. The following Figure 5.24 shows the stacked 400 MHz  $^1\text{H}$  NMR spectrum of crude reaction products from oligomerization reaction conducted at 60 °C, 80 °C and 100 °C respectively.

Referring to Figure 5.24, when the oligomerization reaction was conducted at 60 °C, the alkene groups were not fully converted to epoxide group (compared to 100 °C). The  $^1\text{H}$  NMR spectrum indicates that some of the alkene has been converted to an epoxide group ( $\delta = 2.8\text{-}2.9$  ppm) and these epoxide groups would eventually be ring

opened by the carboxylic group to form estolide oligomers if the reaction time was prolonged. This indicates that at 60 °C the rate of oligomerization is very slow.

When the reaction was conducted at 80 °C, the alkene was fully converted to other functionalities. The  $^1\text{H}$  NMR spectrum shows similar peaks to those observed at 100 °C ( $\delta = 3.7$  ppm, 4.85 ppm), which correspond to estolides. However, the  $^1\text{H}$  NMR spectrum also shows a residual peak at  $\delta = 2.85$  ppm corresponding to the epoxide group. This means that at 80 °C, the oligomerization reaction could proceed to completion if the reaction time was prolonged. Therefore, the most optimum temperature for the oligomerization reaction is 100 °C because all alkene were converted to ester linkages of estolides oligomers in the shortest time possible.

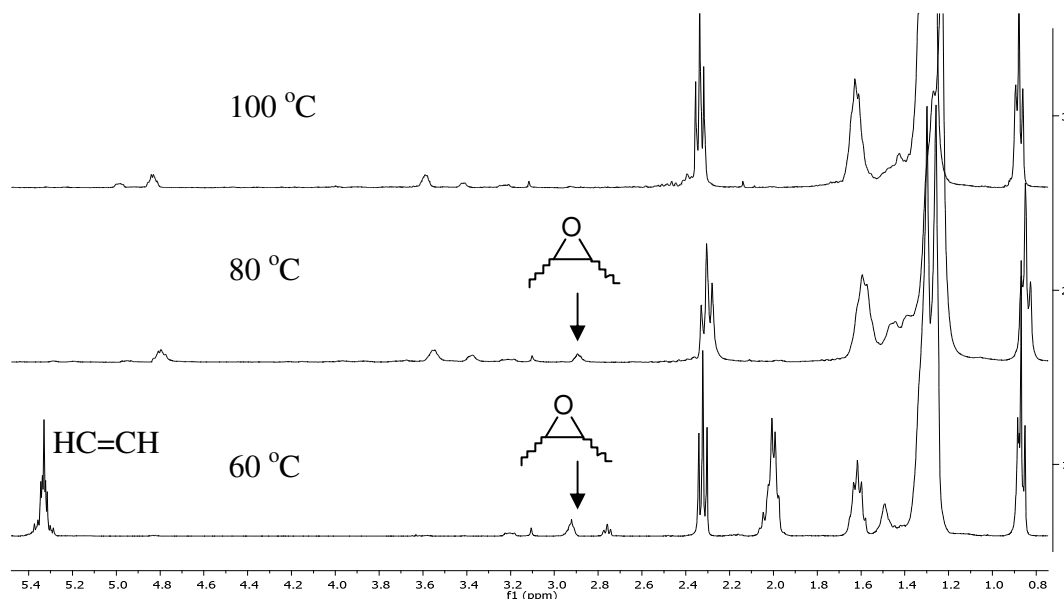


Figure 5.24 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of reaction products in  $\text{CDCl}_3$  from oligomerization reaction conducted at 60 °C, 80 °C and 100 °C respectively

### Effect of hydrogen peroxide : alkene molar ratio on oligomerization

The objective of this study was to determine the optimum molar ratio between  $\text{H}_2\text{O}_2$  and the alkene functionality of the fatty acid. Three ratios were chosen (5:1, 2.5:1 and 1.5:1). When the ratio was lowered from 5:1 down to 2.5:1 ( $\text{H}_2\text{O}_2$ : C=C), the  $^1\text{H}$  NMR spectrum (Figure 5.25) showed that the amount of  $\text{H}_2\text{O}_2$  was enough to fully convert all the alkene to oligomers as the alkene peak at  $\delta = 5.35$  ppm was not visible in the spectrum. However, when the ratio was further lowered to 1.5:1 ( $\text{H}_2\text{O}_2$ : C=C), the  $^1\text{H}$  NMR spectrum showed that the amount of  $\text{H}_2\text{O}_2$  was insufficient to fully convert all the alkene to oligomers. Therefore, the optimum molar ratio was determined as 2.5:1 ( $\text{H}_2\text{O}_2$ : C=C), which is the minimum amount of  $\text{H}_2\text{O}_2$  needed to fully convert alkene to ester linkages of estolides oligomers.

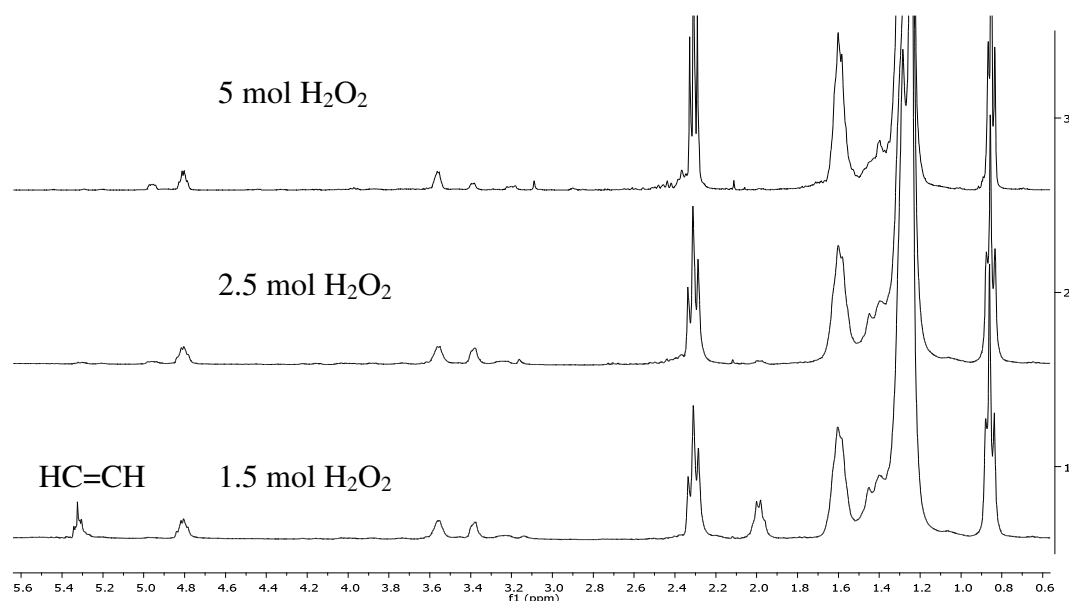


Figure 5.25 Stacked 400 MHz  $^1\text{H}$  NMR spectrum of crude reaction products in  $\text{CDCl}_3$  from oligomerization reaction conducted at 1.5 mol, 2.5 mol and 5 mol of  $\text{H}_2\text{O}_2$  respectively

## 5.5 ONE-POT OLIGOMERIZATION OF OLEIC ACID WITHOUT CATALYST

A report<sup>112</sup> indicated that unsaturated fatty acids such as oleic acid (**5.5**) can be epoxidized in the presence of H<sub>2</sub>O<sub>2</sub> with enzyme (Novozym 435) as the catalyst. The enzyme catalyzed the formation of peracid from the oleic acid with H<sub>2</sub>O<sub>2</sub> as the source of oxygen. The newly formed oleic peracid in turn epoxidized the alkene group of another fatty acid. Based on this procedure, a study was conducted to determine whether (**5.5**) can be “self-epoxidized” without any catalyst (enzymatic or chemical). Therefore, (**5.5**) was reacted with hydrogen peroxide at 80 °C without any catalyst for 1 day in an attempt to yield estolides (**5.6**) and GPC analysis of the crude product showed 43% of oligomers and <sup>1</sup>H NMR spectrum shows some of the alkene group still remained unreacted. Then, the reaction time was prolonged to 3 days (Figure 5.26) in order to increase the oligomeric content and GPC analysis (Table 5.4) indicated that the crude product had about 71% oligomeric content.

Table 5.4 GPC analysis of crude product from oligomerization of oleic acid

Component detected	Gel permeation chromatography (GPC)			Content %
	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI	
1	3300	2800	1.18	38
2	1300	1200	1.05	33
3	480	440	1.09	29

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

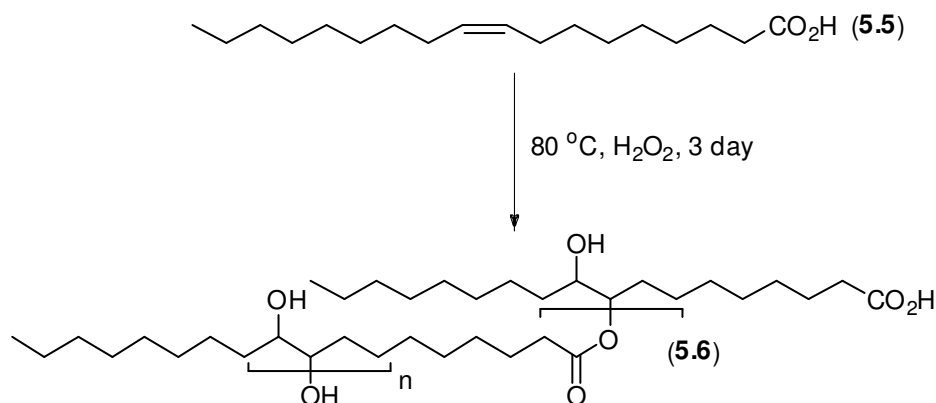


Figure 5.26 Self-oligomerization of oleic acid in the presence of H<sub>2</sub>O<sub>2</sub>

The following Figure 5.27 and 5.28 are the 400 MHz <sup>1</sup>H NMR spectrum and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of the product respectively. Figure 5.27 shows two peaks that correspond to a methine proton attached to a carbon atom of a hydroxyl group (HO-C-H) and an ester group (O=C-O-C-H) at 3.6 ppm and 4.82 ppm respectively. Furthermore, Figure 5.28 analysis shows that both peaks are coupled to each other, which imply that both methine protons are next to each other as depicted in the proposed structure of (**5.6**)

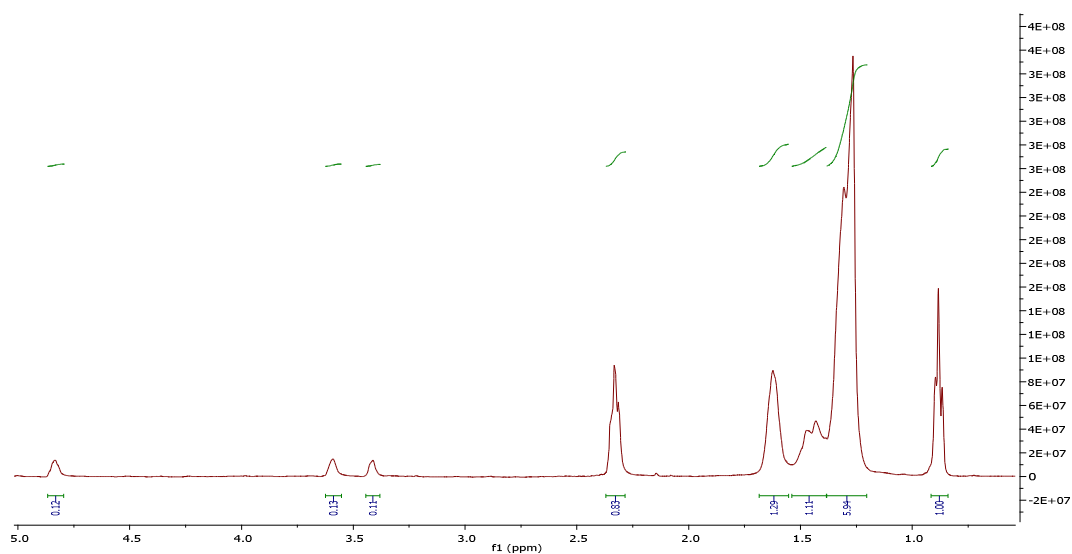


Figure 5.27 400 MHz <sup>1</sup>H NMR spectrum of (**5.6**) in CDCl<sub>3</sub>

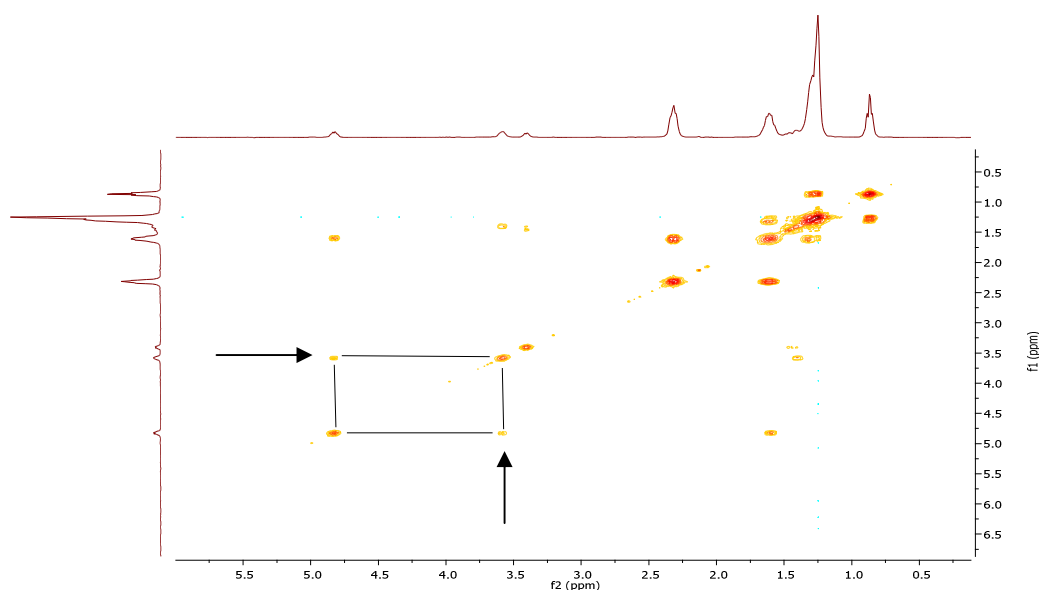


Figure 5.28 400 MHz  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **(5.6)** in  $\text{CDCl}_3$

MALDI-TOF-MS analysis of product (Figure 5.29) shows oligomers of oleic acid with molecular weight of 1829 Da, which corresponds to sodium adduct of hexamer of oleic acid. The repeating unit of the estolides has a molecular weight of 298 Da, which corresponds to structure **(5.19)** depicted in Figure 5.30.

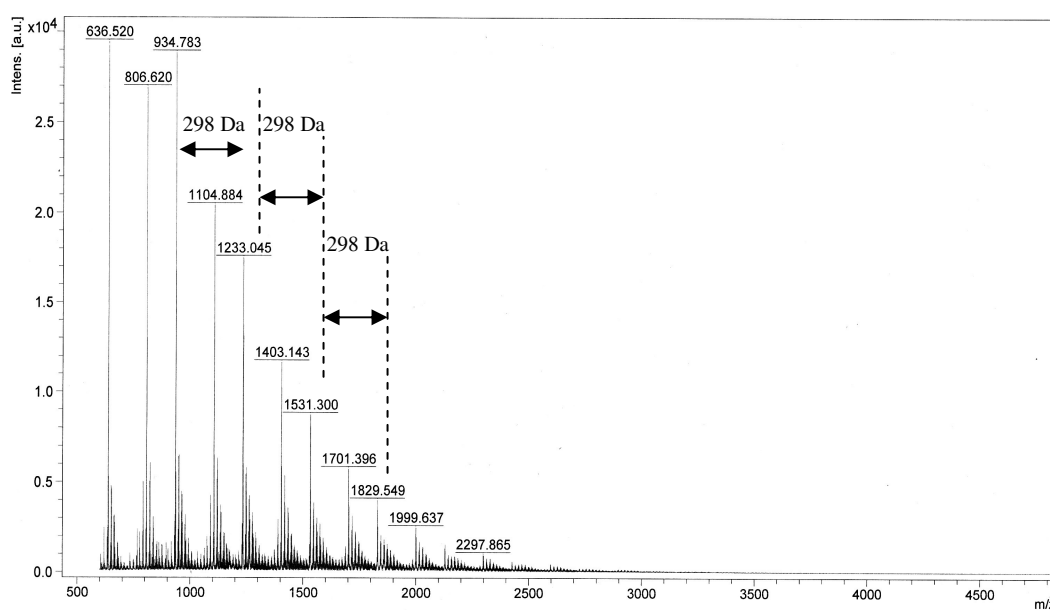


Figure 5.29 MALDI-TOF-MS spectrum of **(5.6)** by using DHB as the matrix in the analysis

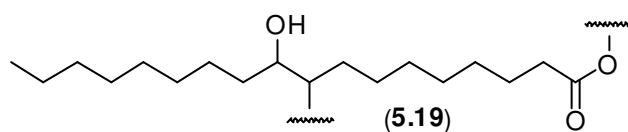
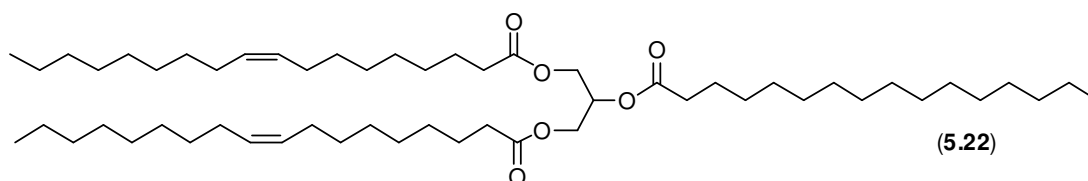
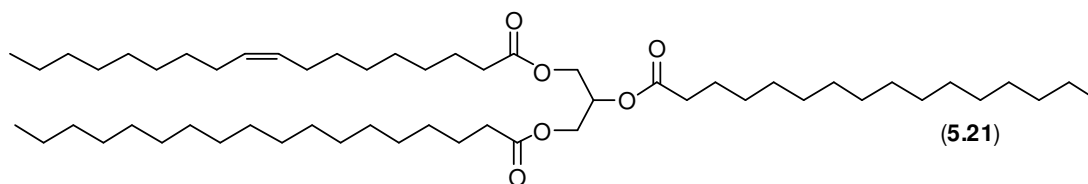


Figure 5.30 Repeating unit of (5.6)

## 5.6 ONE POT OLIGOMERIZATION OF PLANT OIL WITH SUCCINIC ACID

The same method (one-pot oligomerization of oleic acid) was applied to make oligomers from plant oils. The reactions were conducted with succinic acid (5.20) as the substitute for oleic acid in order to incorporate more renewable chemicals into the oligomers. The unsaturated plant oils [cocoa butter (5.21), palm oil (5.22), rapeseed oil (5.23) and soybean oil (5.24)] (Figure 5.31) were used in this study and they were reacted with (5.20) and hydrogen peroxide at 80 °C for 7 days (Figure 5.32). The following Table 5.5 shows the GPC analysis results of the reaction products. Acetic acid was included in this study as a control reaction and it was reacted with (5.24) using the same protocol.





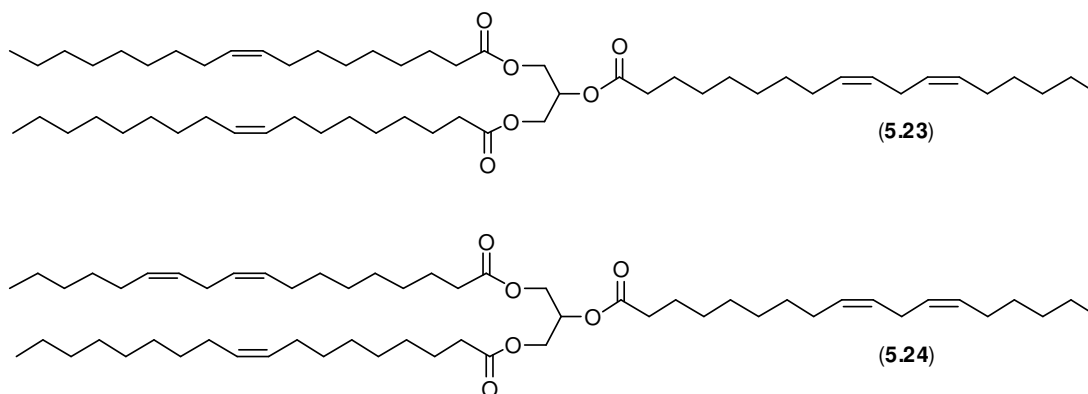


Figure 5.31 Plant oils used in this study

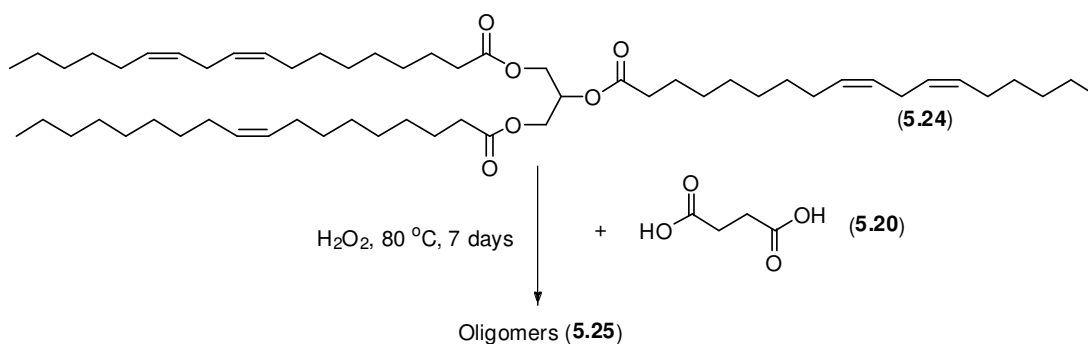


Figure 5.32 Oligomerization of soybean oil (5.24) with succinic acid (5.20) and H<sub>2</sub>O<sub>2</sub> as an example

Table 5.5 GPC analysis of reaction products

Entry	Plant oil	Yield (%)	Gel permeation chromatography		
			M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI
1	Control	25	5100	4400	1.16
2	<b>5.21</b>	0	-	-	-
3	<b>5.22</b>	50	8500	7400	1.15
4	<b>5.23</b>	68	23900	8900	2.70
5	<b>5.24</b>	75	80800	11600	6.97

M<sub>w</sub> = weight average molecular weight, M<sub>n</sub> = number average molecular weight, PDI = polydispersity index

The GPC analysis results shows that the control reaction (Entry 1) only managed to yield 25% oligomeric products and the  $^1\text{H}$  NMR analysis of the products show that (5.24) was majorly converted to epoxidized soybean oil (2.6). Next, the reaction was repeated with cocoa butter (5.21), which has one alkene group per molecule and it was reacted with (5.20) and  $\text{H}_2\text{O}_2$ .  $^1\text{H}$  NMR spectrum of product shows that (5.21) was epoxidized but was not oligomerized as shown by GPC analysis (Entry 2). The (5.21) with only one alkene group per molecule was not reactive to form oligomeric compounds with (5.20) due to the low level of unsaturation.

Palm oil (5.22) which has two alkene groups per molecule was reacted using the same method and the GPC analysis shows that reaction product has about 50% oligomers (Entry 3).  $^1\text{H}$  NMR spectrum of the reaction product shows that the alkene groups of (5.22) were converted to hydroxyl groups. The higher alkene content of (5.22) as compared to (5.21) has contributed to higher amount of oligomers. When (5.22) was substituted with (5.23) which has higher alkene content, the GPC analysis (Entry 4) shows that higher amount of oligomers (68%) was produced as compared to (5.22). As expected, (5.24) produced the highest amount of oligomers (75%) as compared to other plant oils because it has the highest alkene content. This findings support the hypothesis that plant oil with higher alkene content will produce more oligomers. In addition, the higher alkene content of a plant oil also contributed to oligomers with higher molecular weight and PDI.  $^1\text{H}$  NMR analysis of the oligomers (5.25) made from (5.24) (Figure 5.33) shows that all the alkene groups were converted to hydroxyl (3.4 - 3.8 ppm) and esters (4.8 – 4.9 ppm) moieties.

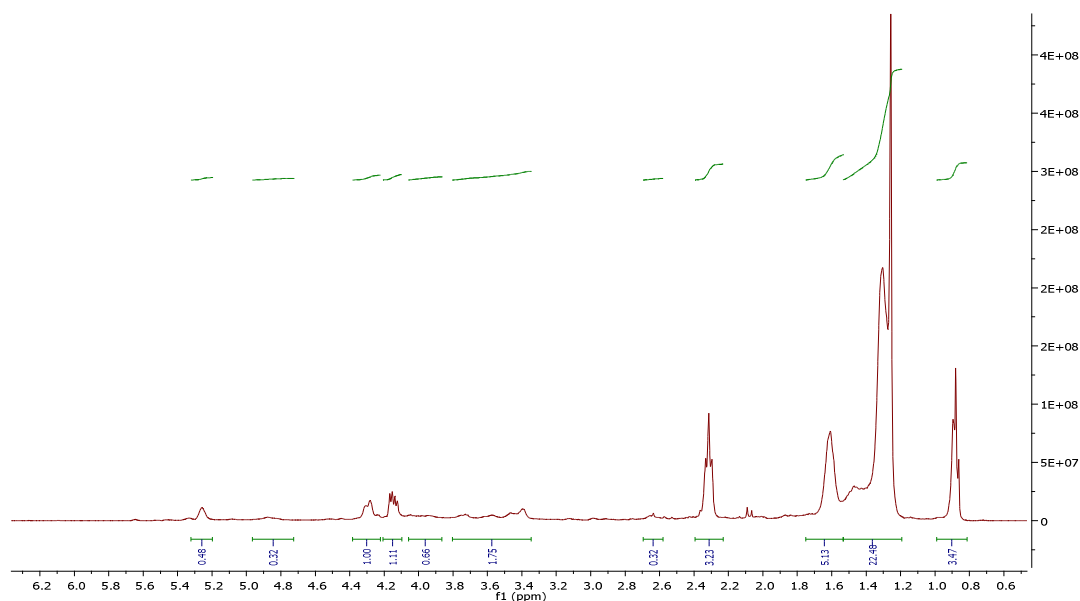


Figure 5.33 400 MHz  $^1\text{H}$  NMR spectrum of oligomers (**5.25**) in  $\text{CDCl}_3$

## 5.7 ONE POT OLIGOMERIZATION OF PLANT OIL WITH ADIPIC ACID AND PHTHALIC ANHYDRIDE

In view that the direct oligomerization of unsaturated plant oils with succinic acid (**5.20**) needed 7 days of reaction time to yield significant amount of oligomers, (**5.20**) was substituted with other dicarboxylic acid to investigate the effect of different dicarboxylic acid on the oligomerization reaction. For this purpose, adipic acid (**5.26**) and phthalic anhydride (**5.27**) were chosen. Adipic acid was chosen because it is a  $\text{C}_6$  linear aliphatic dicarboxylic acid, which has 2 extra  $-\text{CH}_2$  group as compared to (**5.20**).

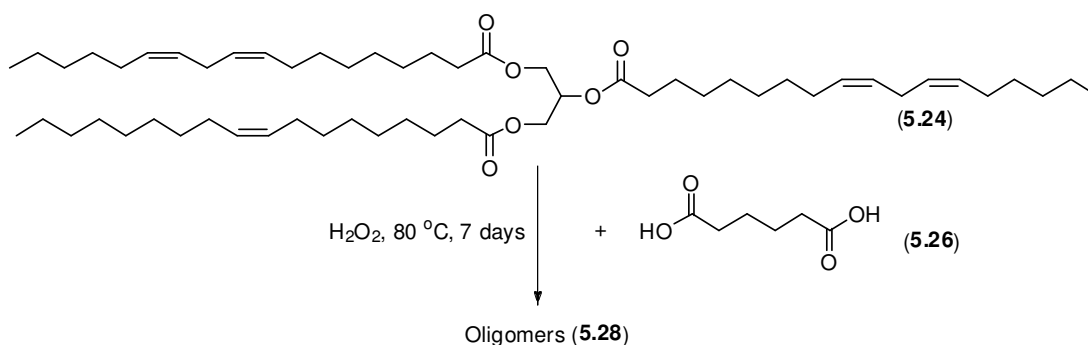


Figure 5.34 Oligomerization of (5.24) with (5.26) and  $\text{H}_2\text{O}_2$

The study was conducted with (5.24) as the plant oil and it was reacted with (5.26) by using same one-pot oligomerization reaction as described in Section 5.6 (page 199) (Figure 5.34).  $^1\text{H}$  NMR analysis of reaction product (5.28) shows that all alkene groups of (5.24) were converted to epoxide as well as hydroxyl groups (Figure 5.35). It also shows that significant amount of epoxide group remained unreacted over the specific duration of reaction, which indicates that (5.26) is less reactive as compared to (5.20) in the oligomerization reaction. In addition, GPC analysis of reaction product shows that the oligomers content was about 40% ( $M_w = 11000$  Da,  $M_n = 8100$  Da,  $\text{PDI} = 1.36$ ), which is significantly lower than product made with (5.20) under similar reaction condition. This may be due to the more hydrophobic nature of longer hydrocarbon chain of (5.26) as compared to (5.20) that made it less effective in an aqueous reaction system.

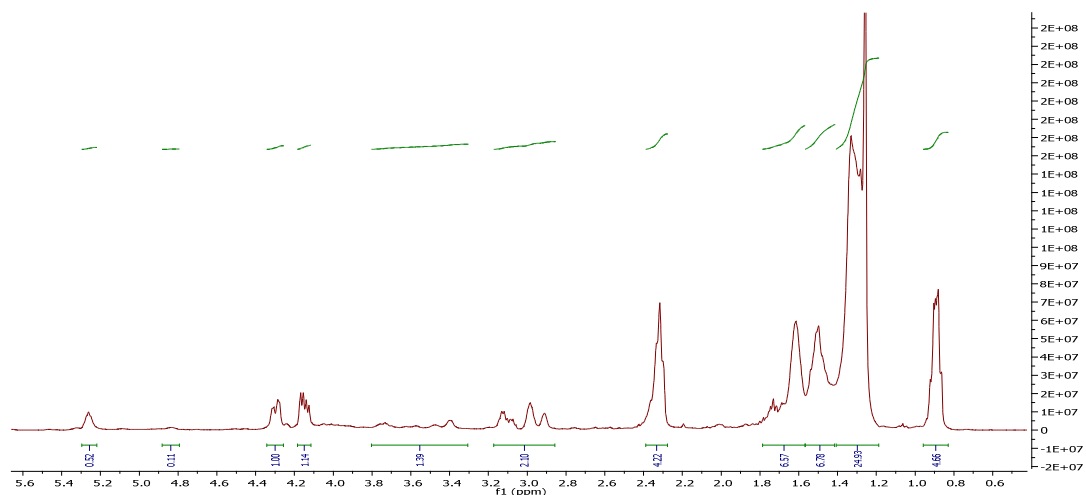


Figure 5.35 400MHz  $^1\text{H}$  NMR spectrum of (**5.28**) in  $\text{CDCl}_3$

When the same reaction was conducted with phthalic anhydride (**5.27**), the reaction was stopped after 1 day because the reaction mixture became too viscous to stir (Figure 5.36). Analysis of the reaction product (**5.29**) with GPC shows that the oligomeric content was about 75% ( $M_w = 20100$  Da,  $M_n = 10100$  Da, PDI = 1.99), which is a significant improvement from earlier studies conducted with (**5.20**). In addition, the reaction time was also significantly reduced from 7 days to 1 day.  $^1\text{H}$  NMR spectrum of (**5.28**) (Figure 5.37) shows the presence of aromatic ring, hydroxyl group and ester group moieties in the product.

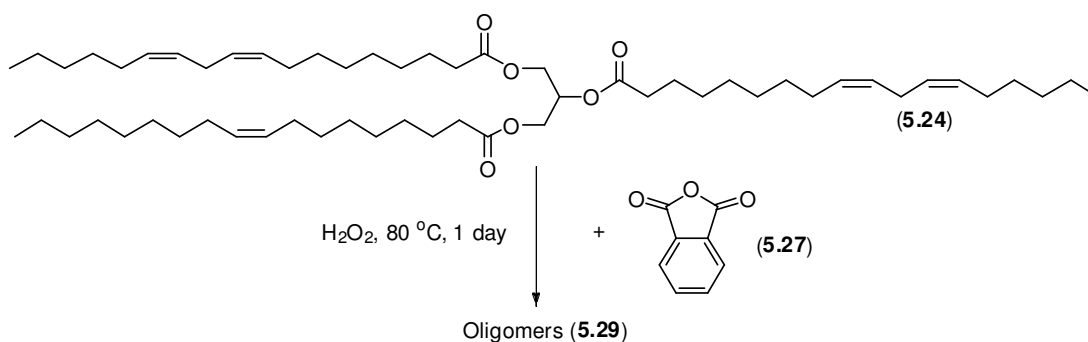


Figure 5.36 Oligomerization of (**5.24**) with (**5.27**) and  $\text{H}_2\text{O}_2$

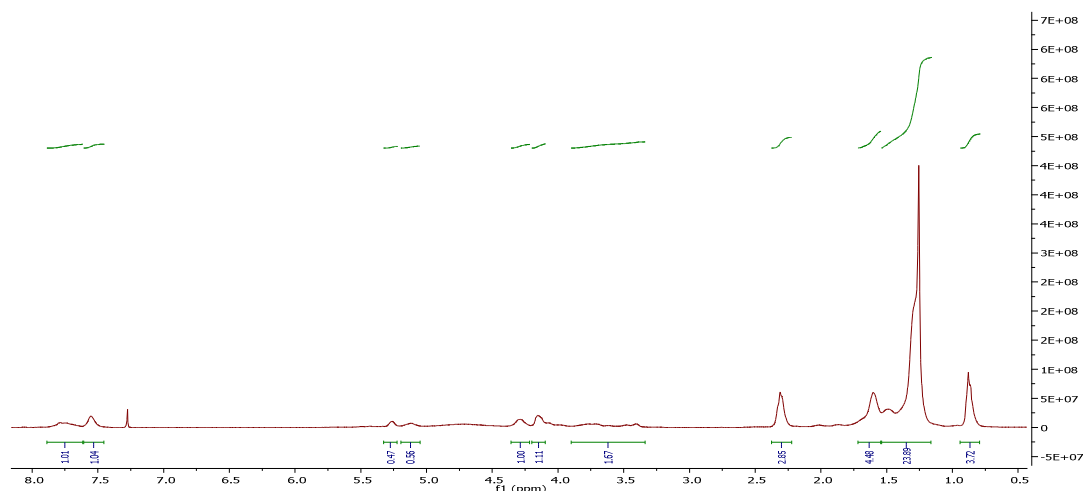


Figure 5.37 400 MHz  $^1\text{H}$  NMR spectrum of (**5.29**) in  $\text{CDCl}_3$

Encouraged by this significant improvement, the same reaction was conducted with palm oil (**5.22**) that has lower level of unsaturation (Figure 5.38). The GPC analysis shows that the reaction product (**5.30**) contains about 66% oligomers ( $M_w = 9200$  Da,  $M_n = 7300$  Da,  $\text{PDI} = 1.26$ ), which is significantly higher than oligomer content produced from reaction system using (**5.20**). Furthermore, the reaction time of was also reduced from 7 days to 1 days when (**5.27**) was used instead of (**5.20**).

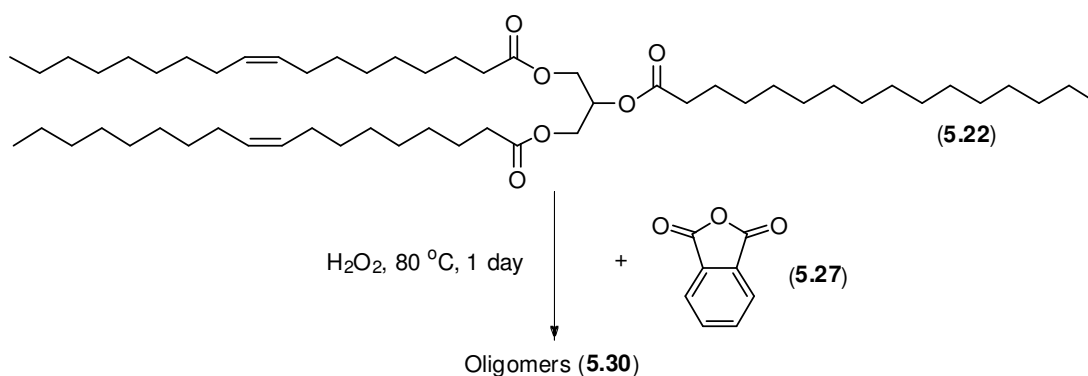


Figure 5.38 Oligomerization of (**5.22**) with (**5.27**) and  $\text{H}_2\text{O}_2$

$^1\text{H}$  NMR spectrum (Figure 5.39) of **(5.30)** shows that all the alkene group of **(5.22)** was converted to hydroxyl moiety and the spectrum also shows that aromatic ring and ester group moieties were present in the product.

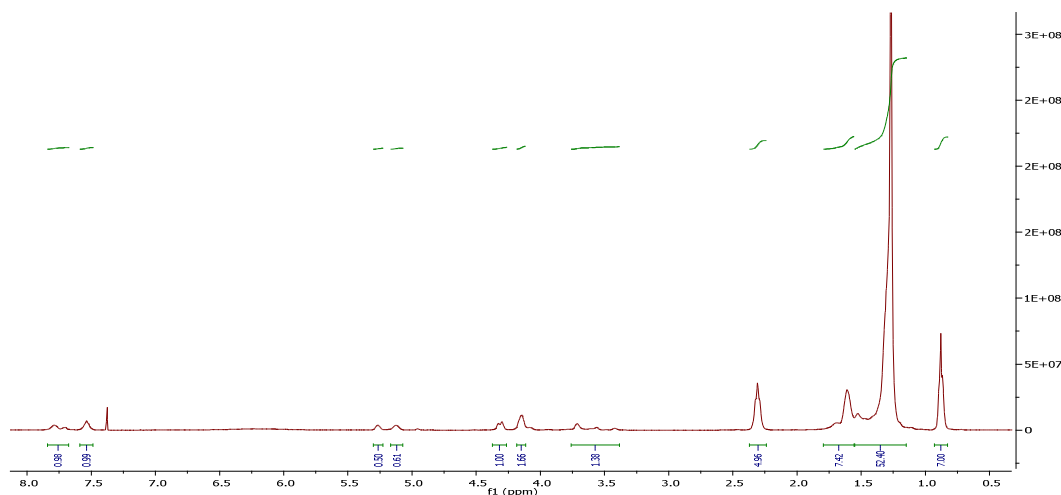


Figure 5.39 400MHz  $^1\text{H}$  NMR spectrum of **(5.30)** in  $\text{CDCl}_3$

## 5.8 POLYURETHANES MADE FROM ESTOLIDES (5.6) AND OLIGOMERS

**(5.25)**

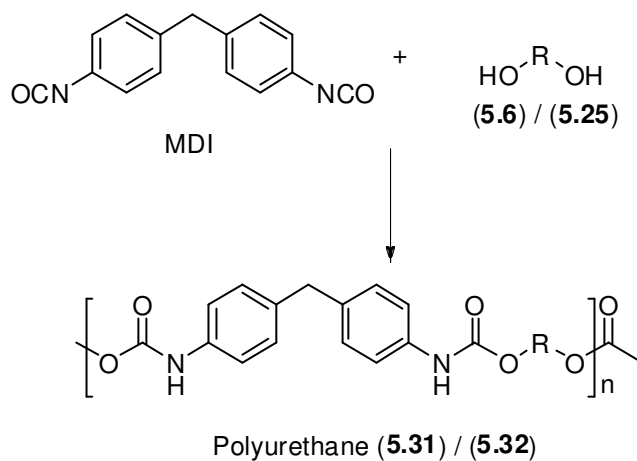


Figure 5.40 Polyurethane made from **(5.6)** and **(5.25)**

The prepared estolides (**5.6**) and oligomers (**5.25**) were reacted with 4,4'-diphenylmethane diisocyanate (MDI) and yielded quantitative amount of PU samples (**5.31**) and (**5.32**) respectively (Figure 5.40). The (**5.31**) and (**5.32**) were cross-linked polymers and were subjected to a tensile test in order to evaluate the strength of these PU samples and the following Figure 5.41 shows the stress-strain curve of (**5.31**) and (**5.32**).

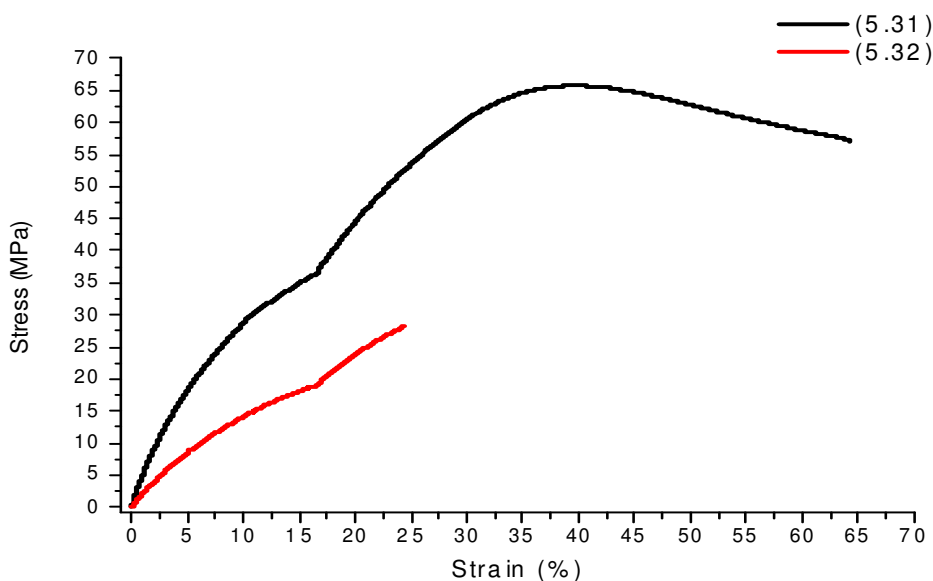


Figure 5.41 Stress-strain curves of (**5.31**) and (**5.32**) according to method EN ISO 529-4: 1997(CEN1997a)

Referring to Figure 5.41, (**5.31**) has high tensile strength (65 MPa) but low elongation at break (64%). These mechanical properties can be attributed to the high cross-link density ( $43 \times 10^{-4} \text{ mol/cm}^3$ ) found in (**5.31**), in which the highly cross-linked (**5.31**) requires more energy to pull it apart and at the same time restricts its elongation. The high cross-link density of (**5.31**) originated from high hydroxyl value of (**5.6**), which is 230 mg KOH/g sample. This range of hydroxyl value is suitable for making rigid PU products such as pipeline insulation materials and adhesives. On the other hand, the hydroxyl value of (**5.25**) was about 144 mg KOH/g sample. This



contributed to the lower cross-link density ( $30 \times 10^{-4} \text{ mol/cm}^3$ ) of PU (**5.32**) and eventually leads to lower tensile strength (28 MPa) and elongation at break (25%).

## 5.9 SUMMARY

When plant oils with varying degree of unsaturation were subjected to one-pot oligomerization reaction in the presence of a tungsten based catalyst and hydrogen peroxide, the amount of oligomers generated from this process was about 20 - 40% depending on the feedstocks and the number average molecular weight of the oligomers ranges from 3000 – 6000 Da. In general, the tungsten catalyzed one-pot oligomerization was not very an effective method to prepare oligomers of plant oil derivatives.

When the same reaction was repeated with oleic acid as the starting material, the reaction products were oligomers of oleic acid (estolides) and analysis with  $^1\text{H}$  NMR reveals that the estolides were linked by ester groups. Further confirmation of the estolides structure was achieved by reduction and saponification reactions. Furthermore, the one-pot oligomerization of oleic acid also yielded azelaic acid as a by-product and data from a series of investigative experiments indicated that the azelaic acid was produced mainly from epoxidized oleic acid before the oligomerization of oleic acid take place.

The oligomerization of oleic acid can also be achieved without any catalyst, in which the oleic acid was “self-epoxidized” by the peracid formed *in situ* from reaction

between itself and  $\text{H}_2\text{O}_2$ . The epoxidized oleic acid was then ring opened by another oleic acid, thus forming the ester linked estolides.

This one-pot catalyst free oligomerization method was applied on various unsaturated plant oils by using renewable dicarboxylic acids such as succinic acid as the epoxidation and epoxide ring-opening agent to oligomerize the unsaturated plant oils. The results show that plant oils with two or more alkene groups per molecule can be oligomerized by succinic acid and the yield of oligomeric products were proportionate with the level of alkene group per molecule.

In comparison with succinic acid, longer chain aliphatic dicarboxylic acid (adipic acid) was less reactive in the oligomerization reaction, in which significant amount of epoxide groups remained unreacted. Meanwhile, aromatic anhydride (phthalic anhydride) was more reactive than succinic acid in the oligomerization procedure and the reaction time was reduced to only 1 day from 7 days. In addition, oligomerization with phthalic anhydride also produced higher amounts of oligomeric products as compared to succinic acid.

The estolides (**5.6**) and oligomers (**5.25**) prepared in this study were used to produce rigid PU by reaction with MDI. Both (**5.6**) and (**5.25**) have relatively high hydroxyl values and gave PU samples with relatively high cross-link density. The high cross-link density restricted the elongation of these PU and also translated to relatively high tensile strength. These PU samples are suitable for making rigid PU for thermal insulation purposes such as pipeline insulation.

## Future Work

The results reported in Chapter 3 and 4 reveal that the properties of PU made from individual plant oil based polyols greatly depends on the level of unsaturation of the plant oils. Generally, plant oil with higher unsaturation level yields PU that exhibits higher tensile strength but lower elongation at break. Based on this structure-property relationship, the blending of plant oils with different level of unsaturation offers a method to tailor the properties of PU made from plant oil based polyols. In addition, the *OP*, *HP* and copolymers of THF can be blended to produce PU with specific properties.

Furthermore, the *OP* can be subjected to saponification reaction to break the ester bond of the oligomerized plant oils and this will yield carboxylic acid groups, which can be reduced to hydroxyl, thus forming *OP* with higher hydroxyl groups that can be used for making rigid PU. The said carboxylic acid groups can also be reacted with diamines to yield non-nylon polyamides or they can be converted to other functionalities that can be used for other applications.

## CHAPTER 6 - EXPERIMENTAL/METHOD

### 6.0 GENERAL INFORMATION AND PROCEDURES

#### Materials

All reactions were performed using commercially available chemicals and the purchased chemicals were used as received without any further purification.

#### General procedure

Thin layer chromatography was carried out on Merck 0.25 mm silica layer foiled-backed 60F-254 TLC sheets developed from potassium permanganate. Column chromatography was performed with Davisil silica gel Grade 633 pore size 60 Å particle size 40-63 µm.

#### Wet chemical analysis of product

All wet chemical analyses were performed according to the AOCS official<sup>117</sup> methods: acid value (AV), Te 1a-64 (89); hydroxyl value (OHV), Cd I3-60(89).

#### Procedure for acid value analysis:

- (a) Weigh 0.5 g of sample into an Erlenmeyer flask.
- (b) Add approximately 100 ml of neutralized solvent (Isopropanol : Toluene, 50:50 mixture) and 3 drops of indicator (1% phenolphthalein in methanol)
- (c) Mix until sample completely dissolved.
- (d) Titrate with standardized alkali solution (0.1 N KOH in ethanol), stirring vigorously to the appearance of the first permanent pink color that persist for 1 minute.

Calculation : Acid value, mg KOH per gram of sample =

$$\frac{\text{volume of alkali, mL} \times N \times 56.1}{\text{mass of sample, g}}$$

where N = normality of alkali determined by standardization.

Procedure for hydroxyl value analysis:

- (a) Weigh 1.0 g of sample into an Erlenmeyer flask.
- (b) Pipet 5.0 ml of pyridine-acetic anhydride reagent (pyridine : acetic anhydride, 3:1) into the flask containing the sample for acetylation. Thoroughly mix the contents by gentle swirling.
- (c) Pipet 5.0 ml of pyridine-acetic anhydride reagent into an empty flask for the reagent blank.
- (d) Place the samples and blank flasks on a hot plate, under a reflux condenser and heat at 100 °C for 1 hour.
- (e) Add 10 ml of water through the condenser to the flask and heat for an additional 10 minute with the reflux condenser attached.
- (f) Allow the flask to cool to room temperature with condenser attached.
- (g) Using a total of about 25 ml of neutralized butyl alcohol, wash the condenser with about 12 ml, remove the condenser and use the remaining butyl alcohol to wash the sides of the flask.
- (h) Add 1 ml of phenolphthalein indicator solution. Titrate to a faint pink end point with 0.5 N alcoholic KOH solution.

Calculation : The hydroxyl value is calculated as follow:

$$\text{Hydroxyl Value} = \frac{B - S \times N \times 56.1}{W}$$

Where

B = volume, ml KOH solution required for the reagent blank

S = volume, ml KOH solution required for titration of the acetylated sample

N = normality of alcoholic KOH determined by standardization

W = mass, gram of sample used for acetylation

### Characterization

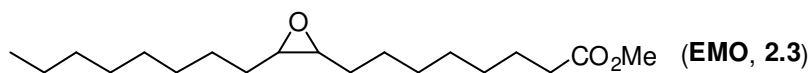
Infrared spectra were recorded as solid or liquid on Perkin-Elmer Spectrum100 FTIR spectrometer and absorption maxima ( $\nu_{\max}$ ) are recorded in wavenumbers ( $\text{cm}^{-1}$ ). Solids were compressed into a thin table and non-volatile liquids were analyzed as thin film over diamond ATR top plate. Mass spectrometry of low resolution was recorded on Bruker Esquire ESI 2000 in which molecular ions, fragment ions and other major peaks are recorded as mass/charge ( $m/z$ ) ratios. High resolution mass spectrometry was achieved by using Bruker MaXis instrument to carry out accurate ESI mass analysis.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy were recorded on Bruker DPX-400 at 400 MHz and 100 MHz respectively at 298K with approximately 10% w/v solutions in deuterated NMR solvents. Chemical shifts are quoted in ppm relatively to internal standard tetramethylsilane (TMS) and reference to the residual solvent. All coupling constant are quoted in hertz (Hz).  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments were routinely confirmed by  $^1\text{H}$ - $^1\text{H}$  (COSY) and  $^1\text{H}$ - $^{13}\text{C}$  (HMQC) data. MALDI-TOF-MS measurement was performed with a Bruker Daltonics Ultraflex II TOF/TOF mass spectrometer equipped with a nitrogen laser delivering 3-ns laser pulses at 337 nm. 5 mg of sample was dissolved in 100  $\mu\text{l}$  tetrahydrofuran and 50 mg of 2,5-dihydroxybenzoic acid (DHB) as the matrix was dissolved in 200  $\mu\text{l}$  tetrahydrofuran. Sample solution (5  $\mu\text{l}$ ) and matrix solution (20  $\mu\text{l}$ ) were mixed and 0.5  $\mu\text{l}$  of this mixture was spotted on the target plate and analyzed. The sample was irradiated with

300-600 pulsed laser shots at a 20% laser power and was measured in reflectron ion mode and was calibrated against poly (ethylene glycol) methyl ether. GPC with THF as the eluent was performed on an Agilent 390-MDS that has an autosampler and a PLgel 5.0  $\mu\text{m}$  bead-size guard column ( $50 \times 7.5$  mm), followed by two linear 5.0  $\mu\text{m}$  bead-size PLgel Mixed D columns ( $300 \times 7.5$  mm) and a differential refractive index detector. Analysis was performed using THF (2% v/v TEA) as the eluent at 30 °C with a flow rate of 1 mL min<sup>-1</sup>. The GPC system was calibrated using linear poly(methyl methacrylate) EasiVial standards (Agilent Ltd.) range from 200 to 10<sup>5</sup> Da and polystyrene EasiVial standards (Agilent Ltd.) range from 162 to 10<sup>5</sup> Da. Data were collected and analyzed using Cirrus GPC/SEC software (version 3.3). Elemental analysis was carried out by Warwick Analytical Services (UK) Ltd. Fatty acid composition analysis by gas chromatography was carried out by Warwick HRI.

## 6.1 GENERAL PROCEDURES FOR SUBSTRATES SYNTHESIZED IN CHAPTER 2

### 6.1.1 General Procedure for the Synthesis of Epoxidized Plant Oil

#### 6.1.1.1 Synthesis of Epoxidized Methyl Oleate (EMO, 2.3) as an example

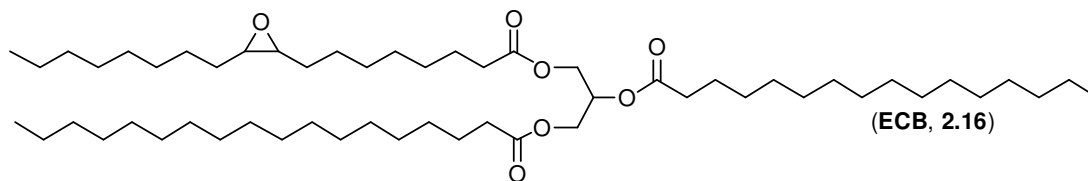


Tungsten powder (12  $\mu\text{m}$ , 99.99%, 6.8 g, 37 mmol), hydrogen peroxide (30% w/w, 50 g, 440 mmol) and deionized water (30 cm<sup>3</sup>) were charged into a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was stirred and heated up to 50 °C until the tungsten powder was totally dissolved, then H<sub>3</sub>PO<sub>4</sub>

(85%, 0.26 g, 2.24 mmol) in water (30 cm<sup>3</sup>) was added into it (this is the tungsten catalyst solution). Methyl oleate (**2.8**) (100 g, 338 mmol) and Adogen 464 (0.45 g, 0.97 mmol) were charged into another 3-neck round bottom flask equipped with a motor stirrer. The methyl oleate mixture was heated to 50 °C and stirred vigorously. The tungsten catalyst solution was added to the methyl oleate mixture followed by deionized water (50 cm<sup>3</sup>), hydrogen peroxide (65 g, 570 mmol). The temperature of the reaction mixture was kept at 70 °C for 3 hours. The reaction mixture was then poured into a separating funnel, and then saturated NaCl solution (100 cm<sup>3</sup>) and diethyl ether (100 cm<sup>3</sup>) were added to the reaction mixture. The aqueous layer was separated from the organic layer and the organic layer was neutralized with saturated sodium hydrogen carbonate solution (50 cm<sup>3</sup>). The organic layer was again washed with NaCl solution (100 cm<sup>3</sup>). The organic layer was dried over anhydrous MgSO<sub>4</sub> followed by removal of solvent *in vacuo* to yield epoxidised methyl oleate (EMO) (97 g, 311 mmol, 92% yield), which was a colorless liquid.  $\nu_{\max}/\text{cm}^{-1}$  2924, 2855 (C-H) 1740 (C=O) 1170 (C-O) 825 (C-O-C) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 3.60 (3H, s, CH<sub>3</sub>O), 3.20-2.80 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.30 (2H, t, *J* = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.67-1.54 (2H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.40 (4H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.37-1.15 (22H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.87 (3H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 174.1 (MeOC=O), 56.8-57.1 (CH<sub>2</sub>CHOCHCH<sub>2</sub>), 51.2 (CH<sub>3</sub>O), 33.7 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.8-28.9 (CH<sub>2</sub>CH<sub>2</sub>), 27.7 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.8 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.5 (CH<sub>2</sub>CH<sub>3</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 335.2562, Found 335.2556

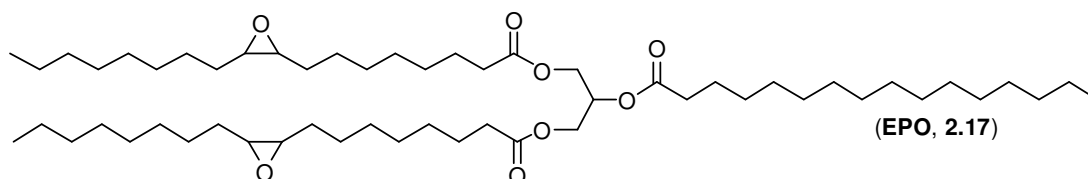


### 6.1.1.2 Synthesis of Epoxidized Cocoa Butter (ECB, 2.16)



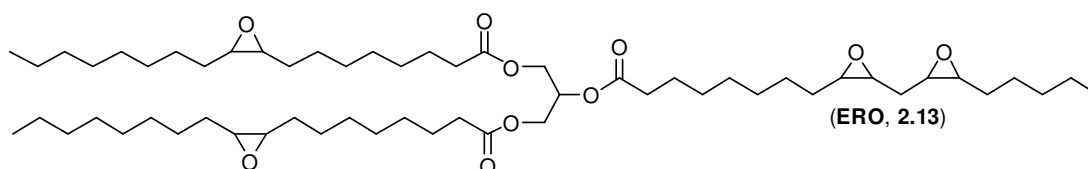
The experiment was conducted according to the procedure described in section 6.1.1.1. Tungsten powder (1.62 g, 8.8 mmol), hydrogen peroxide (30% w/w, 18 g, 160 mmol), deionized water (6 cm<sup>3</sup>), H<sub>3</sub>PO<sub>4</sub> (85%, 1 g, 8.67 mmol), deionized water (16 cm<sup>3</sup>), cocoa butter (**2.9**) (300 g, 349 mmol), Adogen 464 (2.1 g, 4.52 mmol), deionized water (500 cm<sup>3</sup>), hydrogen peroxide (96 g, 850 mmol). Epoxidised cocoa butter (**ECB, 2.16**) (275 g, 324 mmol, 93% yield), pale yellow liquid.  $\nu_{\text{max}}/\text{cm}^{-1}$  2921, 2852 (C-H) 1743 (C=O) 1465 (CH<sub>2</sub>) 1158 and 1113 (C-O) 820 (C-O-C) 721 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.20-5.10 (1H, m, CHO) 4.19 (2H, dd,  $J$ = 11.9 Hz, 4.3 Hz, CH<sub>2</sub>O), 4.02 (2H, dd,  $J$ = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 2.94-2.74 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.18 (6H, t,  $J$ = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.54-1.44 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.42-1.32 (4H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.31-1.08 (72H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.76 (9H, t,  $J$ = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 172.8, 172.4 (C=O), 68.9 ( HC-O), 61.8, 61.6 (H<sub>2</sub>C-O), 56.7 (CH<sub>2</sub>CHOCHCH<sub>2</sub>), 33.9 (O=CCH<sub>2</sub>CH<sub>2</sub>), 29.5-22.7 (CH<sub>2</sub>CH<sub>2</sub>), 27.9 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 899.7680, Found 899.7674

### 6.1.1.3 Synthesis of Epoxidized Palm Oil (EPO, 2.17)



The experiment was conducted according to the procedure described in section 6.1.1.1. Tungsten powder (1.6 g, 8.7 mmol), hydrogen peroxide (30% w/w, 18 g, 160 mmol), deionised water (6 cm<sup>3</sup>), H<sub>3</sub>PO<sub>4</sub> (85%, 1 g, 8.67 mmol), deionized water (16 cm<sup>3</sup>), palm oil (**2.10**) (300 g, 350 mmol), Adogen 464 (2 g, 4.31 mmol), deionized water (450 cm<sup>3</sup>), hydrogen peroxide (90 g, 794 mmol). Epoxidised palm oil (**EPO**, **2.17**) (296 g, 333 mmol, 95% yield), pale yellow liquid.  $\nu_{\text{max}}/\text{cm}^{-1}$  2923, 2854 (C-H) 1742 (C=O) 1464 (CH<sub>2</sub>) 1158 and 1111 (C-O) 821 (C-O-C) 722 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.28-5.21 (1H, m, CHO) 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.2 Hz, CH<sub>2</sub>O), 4.13 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.10-2.80 (4H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.30 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.65-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.55-1.42 (8H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.42-1.20 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.89 (9H, t,  $J$  = 7.5 Hz CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 172.9, 172.5 (C=O), 68.8 ( HC-O), 61.8, 61.5 (H2C-O), 56.5 (CH<sub>2</sub>CHOCHCH<sub>2</sub>), 33.7 (O=CCH<sub>2</sub>CH<sub>2</sub>), 29.4-22.4 (CH<sub>2</sub>CH<sub>2</sub>), 28.9 (CHOCH<sub>2</sub>CH<sub>2</sub>), 27.8 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 913.7467, Found 913.7467

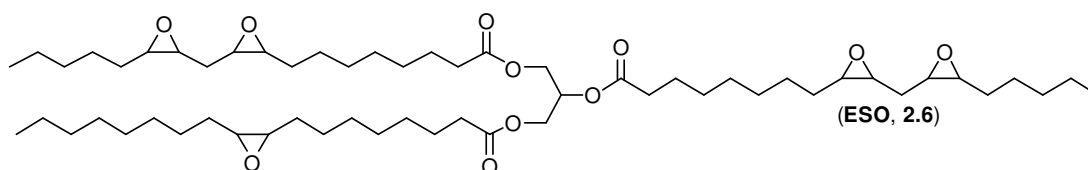
#### 6.1.1.4 Synthesis of Epoxidized Rapeseed Oil (ERO, 2.13)



The experiment was conducted according to the procedure described in section 6.1.1.1. Tungsten powder (1.2 g, 6.52 mmol), hydrogen peroxide (30% w/w, 16 g, 141 mmol), deionized water (4 cm<sup>3</sup>), H<sub>3</sub>PO<sub>4</sub> (85%, 0.8 g, 6.94 mmol), deionized water (8 cm<sup>3</sup>), rapeseed oil (**2.11**) (200 g, 227 mmol), Adogen 464 (1.6 g, 3.45

mmol), deionized water (320 cm<sup>3</sup>), hydrogen peroxide (120 g, 1058 mmol). Epoxidised rapeseed oil (**ERO**, **2.13**) (200 g, 211 mmol, 93% yield), a pale yellow liquid.  $\nu_{\text{max}}/\text{cm}^{-1}$  2924, 2854 (C-H) 1742 (C=O) 1464 (CH<sub>2</sub>) 1155 and 1108 (C-O) 825 (C-O-C) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.20 (1H, m, CHO) 4.31 (2H, dd,  $J$ = 11.9 Hz, 4.2 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$ = 11.9 Hz, 6.0 Hz, CH<sub>2</sub>O), 3.20-3.00 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.97-2.90 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.89-2.82 (4H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.31 (6H, t,  $J$ = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.82-1.68 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 1.66-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.56-1.42 (12H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.40-1.20 (54H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t,  $J$ = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 172.6, 172.3 (C=O), 68.8 ( HC-O), 61.8, 61.7 (HC-O), 56.7, 53.7 (CH<sub>2</sub>CHOCHCH<sub>2</sub>), 33.8 (O=CCH<sub>2</sub>CH<sub>2</sub>), 29.1-22.6 (CH<sub>2</sub>CH<sub>2</sub>), 27.7-26.5 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 969.7365, Found 969.7368

#### 6.1.1.5 Synthesis of Epoxidized Soybean Oil (ESO, 2.6)



The experiment was conducted according to the procedure described in section 6.1.1.1. Tungsten powder (1.8 g, 9.8 mmol), hydrogen peroxide (30% w/w, 24 g, 211 mmol), deionized water (6 cm<sup>3</sup>), H<sub>3</sub>PO<sub>4</sub> (85%, 1.2 g, 10.4 mmol), deionized water (12 cm<sup>3</sup>), soybean oil (**2.12**) (300 g, 341 mmol), Adogen 464 (2.4 g, 5.17 mmol), deionized water (480 cm<sup>3</sup>), hydrogen peroxide (180 g, 1588 mmol). Epoxidised

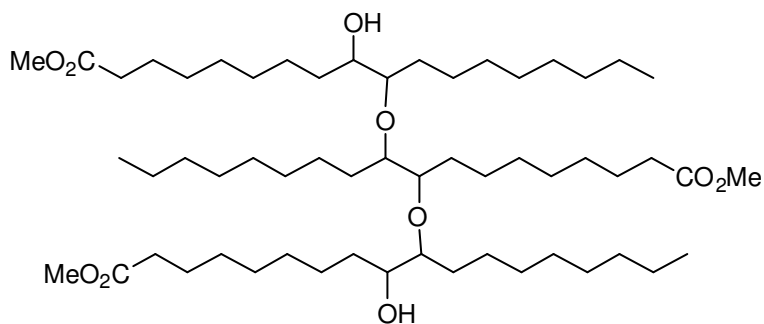
soybean oil (**ESO**, **2.6**) (297 g, 310 mmol, 91% yield), a pale yellow liquid.  $\nu_{\max}/\text{cm}^{-1}$  2923, 2854 (C-H) 1741 (C=O) 1464 (CH<sub>2</sub>) 1154 (C-O) 823 (C-O-C) 724 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.28-5.20 (1H, m, CHO) 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.3Hz, CH<sub>2</sub>O), 4.12 (2H, dd,  $J$  = 11.9 Hz, 6.0 Hz, CH<sub>2</sub>O), 3.16-2.98 (4H, m, CH<sub>2</sub>CHOCHCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.97-2.88 (4H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.88-2.81 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.30 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.82-1.66 (4H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>CHOCHCH<sub>2</sub>), 1.66-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.56-1.42 (12H, m, CHOCHCH<sub>2</sub>CH<sub>2</sub>), 1.42-1.20 (48H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.89 (9H, t,  $J$  = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 172.5, 172.1 (C=O), 68.7 ( HC-O), 61.8, 61.5 (HC-O), 56.5-53.7 (CH<sub>2</sub>CHOCHCH<sub>2</sub>), 33.7 (O=CCH<sub>2</sub>CH<sub>2</sub>), 29.3-22.3 (CH<sub>2</sub>CH<sub>2</sub>), 28.8-22.4 (CHOCHCH<sub>2</sub>CH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.6 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 983.7158, Found 983.7158

## 6.1.2 General Procedure for Oligomerization of Epoxidized Plant Oil without Solvent

### 6.1.2.1 Oligomerization of epoxidized methyl oleate (**2.3**) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O without solvent as an example

Epoxidized methyl oleate (**2.3**) (5 g, 16 mmol) was weighed into a round bottom flask and was heated to 20 °C. It was stirred under N<sub>2</sub> atmosphere for 30 minutes before BF<sub>3</sub>.Et<sub>2</sub>O (0.34 g, 2.4 mmol) was added drop-wise to it. After the addition of BF<sub>3</sub>.Et<sub>2</sub>O was completed, the reaction temperature was maintained at 20 °C under N<sub>2</sub> atmosphere for 24 hours. Then, the reaction mixture was poured into separation funnel and washed with sodium bicarbonate solution (50 ml). The aqueous layer was separated from the organic layer and CHCl<sub>3</sub> (50 ml) was added to organic layer. The

organic layer was dried over anhydrous  $\text{MgSO}_4$  and  $\text{CHCl}_3$  was removed *in vacuo* to yield a yellowish liquid (4.95 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3358 (O-H) 2925, 2855 (C-H) 1738 (C=O) 1460 ( $\text{CH}_2$ ) 1170 (C-O) 724 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 3.67 (9H, s,  $\text{HCO}$ ), 3.60-3.20 (6H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.20 (72H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.9 (9H, t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.8 (C=O) 74.0, 73.2, 71.6 (C-O), 50.8 ( $\text{OCH}_3$ ) 33.6 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 31.1, 29.3, 28.9, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{CH}_2\text{CH}_3$ )  $m/z$  ( $\text{ES}^+$ ),  $[\text{M}+\text{Na}]$ , Required 977.7991, Found 977.7991



#### 6.1.2.2 Oligomerization of epoxidized cocoa butter (**2.16**) catalyzed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ without solvent

The experiment was conducted according to the procedure described in section 6.1.2.1. Epoxidized cocoa butter (**2.16**) (5 g, 5.7 mmol),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.13 g, 0.9 mmol); a yellowish viscous liquid (4.9 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2916, 2849 (C-H) 1739 (C=O) 1466 ( $\text{CH}_2$ ) 1164 (C-O) 721 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.28-5.25 (1H, m,  $\text{CHO}$ ), 4.29 (2H, dd,  $J$  = 11.8 Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.85-3.25 (2H, m,  $\text{CHO}$ ), 2.35 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.65-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.45-1.15 (72H, m,  $\text{CH}_2\text{CH}_2$ ), 0.9 (9H, t,  $J$  =

7.5Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.3, 172.8 (C=O) 72.5 (HC-O) 68.8 (HC-O), 61.9, 62.0 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 24.7 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.6, 23.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### **6.1.2.3 Oligomerization of epoxidized palm oil (2.17) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O without solvent**

The experiment was conducted according to the procedure described in section 6.1.2.1. Epoxidized palm oil (**2.17**) (5 g, 5.6 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.23 g, 1.65 mmol). The reactant mixture gel-up / polymerized as soon as BF<sub>3</sub>.Et<sub>2</sub>O was added to it. The polymerized product was sticky and rubbery. ν<sub>max</sub>/cm<sup>-1</sup> 3326 (O-H) 2916, 2849 (C-H) 1740 (C=O) 1462 (CH<sub>2</sub>) 1160 (C-O) 720 (CH<sub>2</sub>)

#### **6.1.2.4 Oligomerization of epoxidized rapeseed oil (2.13) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O without solvent**

The experiment was conducted according to the procedure described in section 6.1.2.1. Epoxidized rapeseed oil (**2.13**) (5 g, 5.3 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.45 g, 3.17 mmol). The reactant mixture gel-up / polymerized as soon as BF<sub>3</sub>.Et<sub>2</sub>O was added to it. The polymerized product was sticky and rubbery. ν<sub>max</sub>/cm<sup>-1</sup> 3348 (O-H) 2920, 2853 (C-H) 1741 (C=O) 1463 (CH<sub>2</sub>) 1165 (C-O) 721 (CH<sub>2</sub>)

#### **6.1.2.5 Oligomerization of epoxidized soybean oil (2.6) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O without solvent**

The experiment was conducted according to the procedure described in section 6.1.2.1. Epoxidized soybean oil (**2.6**) (5 g, 5.2 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.55 g, 3.9 mmol). The reactant mixture gel-up / polymerized as soon as BF<sub>3</sub>.Et<sub>2</sub>O was added to it. The

polymerized product was sticky and rubbery.  $\nu_{\text{max}}/\text{cm}^{-1}$  3334 (O-H) 2922, 2856 (C-H) 1738 (C=O) 1460 (CH<sub>2</sub>) 1171 (C-O) 723 (CH<sub>2</sub>)

#### **6.1.2.6 Oligomerization of euphorbia oil (2.18) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O without solvent**

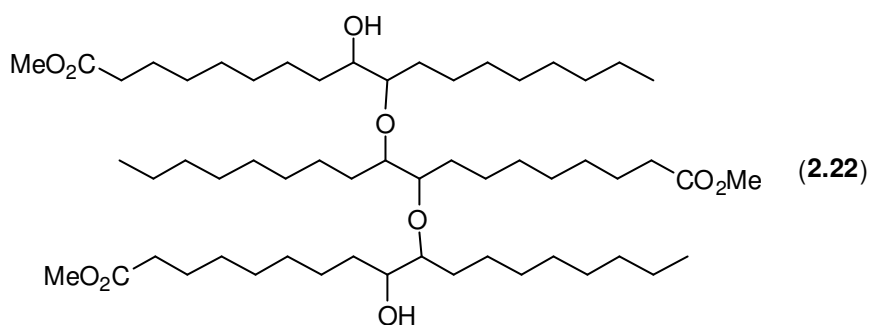
The experiment was conducted according to the procedure described in section 6.1.2.1. Euphorbia oil (**2.18**) (5 g, 5.5 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.23 g, 1.65 mmol). The reactant mixture gel-up / polymerized as soon as BF<sub>3</sub>.Et<sub>2</sub>O was added to it. The polymerized product was sticky and rubbery.  $\nu_{\text{max}}/\text{cm}^{-1}$  3340 (O-H) 2924, 2855 (C-H) 1742 (C=O) 1458 (CH<sub>2</sub>) 1160 (C-O) 736 (CH<sub>2</sub>)

#### **6.1.3 General Procedure for Oligomerization of Epoxidized Plant Oil with Solvent**

##### **6.1.3.1 Oligomerization of epoxidized methyl oleate (2.3) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O with solvent as an example**

Epoxidized methyl oleate (**2.3**) (100 g, 320 mmol) was weighed into a round bottom flask and hexane (200 ml) was added to it. The reactants mixture was stirred and heated at 20 °C under N<sub>2</sub> atmosphere for 30 minutes before BF<sub>3</sub>.Et<sub>2</sub>O (2.3 g, 16 mmol) was added drop-wise to (**2.3**). After the addition of BF<sub>3</sub>.Et<sub>2</sub>O was completed, the reaction temperature was maintained at 20 °C for another 24 hours. Then, the reaction mixture was poured into separation funnel and washed with sodium bicarbonate solution (250 ml). The aqueous layer was separated from the organic layer and CHCl<sub>3</sub> (500 ml) was added to organic layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and CHCl<sub>3</sub> was removed *in vacuo* to yield a yellowish liquid

(**2.22**) (95.24 g);  $\nu_{\max}/\text{cm}^{-1}$  3350 (O-H) 2922, 2853 (C-H) 1739 (C=O) 1459 ( $\text{CH}_2$ ) 1169 (C-O) 723 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 3.66 (9H, s,  $\text{HCO}$ ), 3.60-3.05 (6H, m,  $\text{HCO}$ ), 2.30 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.20 (72H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.87 (9H, t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.9 (C=O) 74.1, 73.4, 71.7 (C-O), 58.8 ( $\text{OCH}_3$ ) 33.6 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.3, 28.9, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{CH}_2\text{CH}_3$ )  $m/z$  ( $\text{ES}^+$ ),  $[\text{M}+\text{Na}^+]$ , Required 977.7991, Found 977.7989



#### 6.1.3.2 Oligomerization of epoxidized cocoa butter (**2.16**) catalyzed by $\text{BF}_3 \cdot \text{Et}_2\text{O}$ with solvent

The experiment was conducted according to the procedure described in section 6.1.3.1. Epoxidized cocoa butter (**2.16**) (50 g, 57 mmol), hexane (80 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.81 g, 5.7 mmol), a yellowish liquid (**2.23**, 49.3 g);  $\nu_{\max}/\text{cm}^{-1}$  3360 (O-H) 2918, 2850 (C-H) 1740 (C=O) 1468 ( $\text{CH}_2$ ) 1165 (C-O) 722 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.23-5.15 (1H, m,  $\text{CHO}$ ), 4.24 (2H, dd,  $J$  = 11.7 Hz, 3.7 Hz,  $\text{CH}_2\text{O}$ ), 4.07 (2H, dd,  $J$  = 11.9 Hz, 6.0 Hz,  $\text{CH}_2\text{O}$ ), 3.60-3.10 (2H, m,  $\text{HCO}$ ), 2.26 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.62-1.47 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.45-1.10 (72H, m,  $\text{CH}_2\text{CH}_2$ ), 0.82 (9H, t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  =



173.1, 172.6 (C=O) 72.5 ( $\text{HC-O}$ ) 68.7 ( $\text{HC-O}$ ), 61.9, 61.7 ( $\text{H}_2\text{C-O}$ ), 33.8 ( $\text{O=CCH}_2$ ), 24.6 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 29.6, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.3.3 Oligomerization of epoxidized palm oil (**2.17**) catalyzed by $\text{BF}_3\cdot\text{Et}_2\text{O}$ with solvent

The experiment was conducted according to the procedure described in section 6.1.3.1. Epoxidized palm oil (**2.17**) (100 g, 112 mmol), hexane (600 ml),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (1.1 g, 7.8 mmol), a yellowish liquid (**2.24**, 98.4 g);  $\nu_{\text{max}}/\text{cm}^{-1}$  3348 (O-H) 2921, 2851 (C-H) 1742 (C=O) 1459 ( $\text{CH}_2$ ) 1158 (C-O) 722 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.22-5.13 (1H, m,  $\text{CHO}$ ), 4.21 (2H, dd,  $J$  = 11.9 Hz, 4.1 Hz,  $\text{CH}_2\text{O}$ ), 4.07 (2H, dd,  $J$  = 11.8 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.80-3.00 (4H, m,  $\text{HCO}$ ), 2.23 (6H, t,  $J$  = 7.5 Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.60-1.47 (6H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 1.35-1.10 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.79 (9H, t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.2, 172.5 (C=O) 72.4 ( $\text{HC-O}$ ) 68.8 ( $\text{HC-O}$ ), 61.8, 61.6 ( $\text{H}_2\text{C-O}$ ), 33.9 ( $\text{O=CCH}_2$ ), 24.7 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 29.5, 22.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.3.4 Oligomerization of epoxidized rapeseed oil (**2.17**) catalyzed by $\text{BF}_3\cdot\text{Et}_2\text{O}$ with solvent

The experiment was conducted according to the procedure described in section 6.1.3.1. Epoxidized rapeseed oil (**2.13**) (50 g, 53 mmol), dry dichloromethane (500 ml),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0.60 g, 4.24 mmol), a yellowish liquid (**2.25**, 49.5 g);  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2920, 2851 (C-H) 1728 (C=O) 1459 ( $\text{CH}_2$ ) 1072 (C-O) 752 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.35-5.21 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.6 Hz, 5.6 Hz,  $\text{CH}_2\text{O}$ ), 3.80-3.05 (8H, m,  $\text{HCO}$ ), 2.35 (6H, t,  $J$  = 7.5 Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.70-1.55 (6H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 1.42-1.12 (54H, m,

CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t,  $J = 7.5$  Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_C =$  173.1, 172.7 (C=O), 68.8 (HC-O), 65.6 (HC-O), 61.2, 61.8 (H<sub>2</sub>C-O), 33.8 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.1, 29.4, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.3.5 Oligomerization of epoxidized soybean oil (**2.6**) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O with solvent

The experiment was conducted according to the procedure described in section 6.1.3.1. Epoxidized soybean oil (**2.6**) (50 g, 53 mmol), dry dichloromethane (500 ml), BF<sub>3</sub>.Et<sub>2</sub>O (1.01 g, 7.1 mmol), a yellowish liquid (**2.26**, 49 g)  $\nu_{\max}/\text{cm}^{-1}$  3360 (O-H) 2922, 2853 (C-H) 1740 (C=O) 1458 (CH<sub>2</sub>) 1075 (C-O) 754 (CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_H =$  5.29-5.20 (1H, m, CH<sub>2</sub>O), 4.30 (2H, dd,  $J = 11.7$  Hz, 3.9 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J = 11.3$  Hz, 5.6 Hz, CH<sub>2</sub>O), 3.90-3.05 (10H, m, HCO), 2.31 (6H, t,  $J = 7.5$  Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.51 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.50-1.20 (48H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t,  $J = 7.5$  Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_C =$  172.9, 172.5 (C=O), 73.4 (HC-O), 68.7 (HC-O), 61.7, 61.9 (H<sub>2</sub>C-O), 33.7 (O=CCH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.1, 22.4, 15.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.7 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.3.6 Oligomerization of euphorbia oil (**2.18**) catalyzed by BF<sub>3</sub>.Et<sub>2</sub>O with solvent

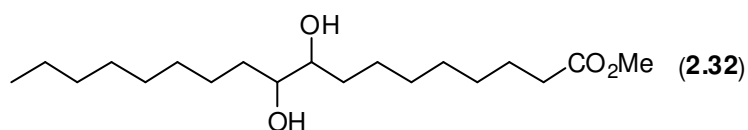
The experiment was conducted according to the procedure described in section 6.1.3.1. Euphorbia oil (**2.18**) (70 g, 77 mmol), dry dichloromethane (140 ml), BF<sub>3</sub>.Et<sub>2</sub>O (0.7 g, 5.0 mmol), a yellowish liquid (**2.27**, 50 g);  $\nu_{\max}/\text{cm}^{-1}$  3481 (O-H) 2924, 2854 (C-H) 1742 (C=O) 1464 (CH<sub>2</sub>) 1161 (C-O) 756 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_H =$  5.58-5.29 (6H, m, CH=CH), 5.28-5.23 (1H, m, CHO), 4.29 (2H,

dd,  $J = 11.8$  Hz,  $3.9$  Hz,  $\text{CH}_2\text{O}$ ),  $4.14$  (2H, dd,  $J = 11.7$  Hz,  $5.5$  Hz,  $\text{CH}_2\text{O}$ ),  $3.75 - 3.10$  (4H, m,  $\text{HCO}$ ),  $2.30$  (6H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ),  $2.10-1.95$  (12H, m,  $\text{CH}_2\text{CH}=\text{CH}$ )  $1.67-1.54$  (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ),  $1.50-1.20$  (50H, m,  $\text{CH}_2\text{CH}_2$ ),  $0.88$  (9H, t,  $J = 6.9$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.2$ ,  $172.8$  ( $\text{C}=\text{O}$ ),  $129.7$ ,  $125.5$  ( $\text{HC}=\text{CH}$ ),  $74.6$ ,  $73.7$  ( $\text{HC}-\text{O}$ ),  $68.8$  ( $\text{HC}-\text{O}$ ),  $62.0$ ,  $61.9$  ( $\text{H}_2\text{C}-\text{O}$ ),  $33.9$  ( $\text{O}=\text{CCH}_2$ ),  $27.1$  ( $\text{CH}_2\text{CH}=\text{CH}$ ),  $24.6$  ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ),  $29.4$ ,  $22.7$  ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ),  $13.8$  ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.4 Synthesis of dihydroxy methyl stearate (2.32) (DHMS)

Epoxidized methyl oleate (**2.3**) (57.6 g, 184 mmol) was weighed into a round bottom flask. Deionized water (50 ml) and  $\text{H}_3\text{PO}_4$  (1 g, 10 mmol) were added to (**2.3**). The mixture was stirred and heated to  $80^\circ\text{C}$  for 12 hours. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml),  $\text{NaHCO}_3$  (100 ml) and NaCl (100 ml). The aqueous layer was discarded and  $\text{CHCl}_3$  (100 ml) was added to the organic layer. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and  $\text{CHCl}_3$  was removed *in vacuo* to yield a colorless liquid. The colorless liquid was dissolved in hot hexane ( $60^\circ\text{C}$ , 60 ml) and the mixture was left to cool to room temperature. White precipitate was formed from the mixture upon cooling and was filtered and washed with hexane to yield white solid (**2.32**, 33.0 g, 100 mmol, 54% yield).  $\nu_{\text{max}}/\text{cm}^{-1}$  3342 (O-H) 2912, 2846 (C-H) 1742 ( $\text{C}=\text{O}$ ) 1467 ( $\text{CH}_2$ ) 1166, 1038 (C-O) 720 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 3.67$  (3H, s,  $\text{HCO}$ ),  $3.46-3.35$  (2H, m,  $\text{HCO}$ ),  $2.31$  (2H, t,  $J = 7.5$  Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ),  $1.68-1.56$  (2H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ),  $1.55-1.39$  (4H, m,  $\text{HOCCCH}_2$ ),  $1.37-1.20$  (20H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ),  $0.88$  (3H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 174.4$  ( $\text{C}=\text{O}$ )  $74.3$  (C-O),  $51.3$  ( $\text{OCH}_3$ )  $33.8$  ( $\text{O}=\text{CCH}_2$ ),  $33.2$  ( $\text{HOCCCH}_2$ ),  $24.6$  ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ),

31.3, 29.4, 22.9 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ );  $m/z$  ( $\text{ES}^+$ ) [ $\text{M}+\text{Na}^+$ ] Required 353.2662, Found 353.2662; Melting point: 65-67 °C (literature<sup>118</sup> 67-68 °C).

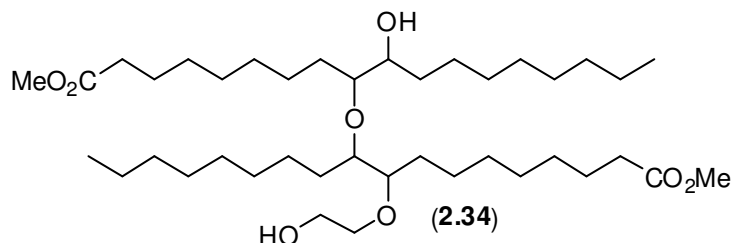


## 6.1.5 General Procedure for Ring Opening of Epoxidized Plant Oil with Polyhydric Alcohol

### 6.1.5.1 Ring opening of epoxidized methyl oleate (2.3) with ethylene glycol as an example

Ethylene glycol (1.5 g, 24 mmol) was stirred and heated to 60 °C in a round bottom flask for 30 minutes before  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.34 g, 2.4 mmol) was added to it. The mixture was stirred and heated at 60 °C for another 30 minutes. Epoxidized methyl oleate (**(2.3)**) (5 g, 16 mmol) was stirred and heated to 60 °C in another round bottom flask. The mixture of ethylene glycol /  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was added drop-wise to (**(2.3)**). After the addition was completed, the reaction temperature was maintained at 60 °C for 24 hours. Then, the reaction mixture was poured into separation funnel and washed with sodium bicarbonate solution (50 ml). The aqueous layer was separated from the organic layer and  $\text{CHCl}_3$  (50 ml) was added to organic layer. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and  $\text{CHCl}_3$  was removed *in vacuo* to yield a yellowish liquid (**(2.34)**, 5.1 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3431 (O-H) 2924, 2854 (C-H) 1738 (C=O) 1457 ( $\text{CH}_2$ ) 1076 (C-O) 723 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 4.19 (2H, t,  $J$ = 7.5 Hz,  $\text{H}_2\text{CO}$ ), 3.80 (2H, t,  $J$ = 7.5 Hz,  $\text{H}_2\text{CO}$ ), 3.68 (6H, s,  $\text{H}_3\text{CO}$ ), 3.60-3.10 (4H, m,  $\text{HCO}$ ), 2.32 (4H, t,  $J$ = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.70-1.56 (4H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.20 (48H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.87 (6H, t,  $J$ = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ )  $^{13}\text{C}$  NMR (100 MHz

CDCl<sub>3</sub>):  $\delta_C$  = 174.1 (C=O), 72.5, 71.5 (C-O), 65.6 (H<sub>2</sub>C-O), 60.6 (H<sub>2</sub>C-O), 51.2 (H<sub>3</sub>C-O) 33.8 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.4, 29.3, 28.9, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>), [M+Na<sup>+</sup>], Required 709.5589 Found 709.5589



#### 6.1.5.2 Ring opening of epoxidized cocoa butter (2.16) with ethylene glycol

The experiment was conducted according to the procedure described in section 6.1.5.1. Ethylene glycol (0.56 g, 9 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.13 g, 0.9 mmol), epoxidized cocoa butter (**2.16**) (5 g, 6 mmol), a viscous yellowish liquid (4.95 g)  $\nu_{\max}/\text{cm}^{-1}$  3380 (O-H) 2916, 2850 (C-H) 1742 (C=O) 1467 (CH<sub>2</sub>) 1162 (C-O) 719 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_H$  = 5.21-5.11 (1H, m, CH<sub>2</sub>O), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.2 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$  = 11.8 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.90-3.25 (4H, m, HCO), 2.23 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.60-1.45 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.42-0.95 (72H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.79 (9H, t,  $J$  = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_C$  = 173.1, 172.7 (C=O) 72.9, 72.6, 71.8 (HC-O) 68.5 (HC-O), 61.8, 61.9 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 22.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.5.3 Ring opening of epoxidized palm oil (2.17) with ethylene glycol

The experiment was conducted according to the procedure described in section 6.1.5.1. Ethylene glycol (1.05 g, 17 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.23 g, 1.65 mmol), epoxidized palm oil (**2.17**) (5 g, 5.6 mmol), a viscous yellowish liquid (**2.35**, 4.9 g).  $\nu_{\max}/\text{cm}^{-1}$  3450 (O-H) 2922, 2854 (C-H) 1742 (C=O) 1465 (CH<sub>2</sub>) 1161, 1096 (C-O)

755 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.30-5.20 (1H, m, CHO), 4.30 (2H, dd, *J* = 11.7 Hz, 3.6 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.8 Hz, 5.8 Hz, CH<sub>2</sub>O), 3.90-3.25 (8H, m, HCO), 2.31 (6H, t, *J* = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.67-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.15 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.86 (9H, t, *J* = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.2, 172.8 (C=O) 72.6, 72.2, 71.6, 68.7, (HC-O), 62.0, 61.8 (H<sub>2</sub>C-O), 33.8 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.5.4 Ring opening of epoxidized rapeseed oil (2.13) with ethylene glycol

The experiment was conducted according to the procedure described in section 6.1.5.1. Ethylene glycol (2.79 g, 45 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.64 g, 4.5 mmol), epoxidized rapeseed oil (**2.13**) (5 g, 5.3 mmol), a viscous yellowish liquid (5.5 g) *v*<sub>max</sub>/cm<sup>-1</sup> 3430 (O-H) 2925, 2856 (C-H) 1739 (C=O) 1463 (CH<sub>2</sub>) 1162, 1097 (C-O) 754 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.30-5.21 (1H, m, CHO), 4.30 (2H, dd, *J* = 11.9 Hz, 4.0 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.6 Hz, 5.7 Hz, CH<sub>2</sub>O), 3.90-3.30 (8H, m, HCO), 2.33 (6H, t, *J* = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.52-1.18 (54H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.0, 172.3 (C=O) 72.7, 69.8, 68.7, 60.8 (HC-O), 62.2, 61.8 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.3, 29.4, 28.8, 22.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

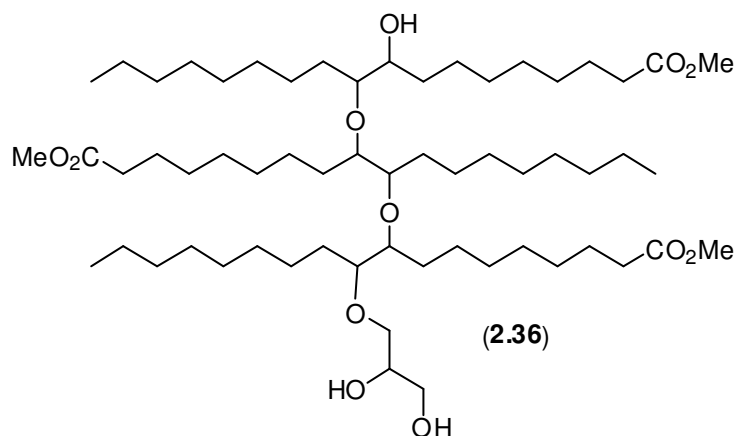
#### 6.1.5.5 Ring opening of epoxidized soybean oil (2.6) with ethylene glycol

The experiment was conducted according to the procedure described in section 6.1.5.1. Ethylene glycol (4.65 g, 75 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (1.06 g, 7.5 mmol), epoxidized soybean oil (**2.6**) (10 g, 10.4 mmol). The reaction mixture polymerized overnight.

$\nu_{\max}/\text{cm}^{-1}$  3459 (O-H) 2924, 2855 (C-H) 1740 (C=O) 1462 (CH<sub>2</sub>) 1164, 1096 (C-O) 753 (CH<sub>2</sub>).

#### 6.1.5.6 Ring opening of epoxidized methyl oleate (2.3) with glycerol

The experiment was conducted according to the procedure described in section 6.1.5.1. Glycerol (9 g, 98 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (1.2 g, 8.5 mmol), epoxidized methyl oleate (**2.3**) (20 g, 64 mmol), a yellowish liquid (**2.36**, 17.3 g).  $\nu_{\max}/\text{cm}^{-1}$  3460 (O-H) 2924, 2854 (C-H) 1739 (C=O) 1458 (CH<sub>2</sub>) 1170, 1075 (C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 3.67 (9H, s, HCO), 3.57-3.10 (11H, m, HCO), 2.28 (6H, t,  $J$  = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.66-1.51 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.49-1.15 (72H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.85 (9H, t,  $J$  = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 174.3 (C=O) 74.2, 73.2, 71.5, 65.1, 63.4, 61.4 (C-O), 51.2 (OCH<sub>3</sub>) 33.8 (O=CCH<sub>2</sub>), 24.7 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.3, 29.4, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>), [M+Na<sup>+</sup>] Required 1051.8359 Found 1051.8359



#### 6.1.5.7 Ring opening of epoxidized cocoa butter (2.16) with glycerol

The experiment was conducted according to the procedure described in section 6.1.5.1. Glycerol (0.83 g, 9 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.13 g, 0.9 mmol), epoxidized cocoa

butter (**2.16**) (5 g, 6 mmol), a viscous yellowish liquid (5 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3360 (O-H) 2920, 2851 (C-H) 1742 (C=O) 1466 (CH<sub>2</sub>) 1163 (C-O) 721 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m, CHO), 4.30 (2H, dd,  $J$ = 11.8 Hz, 3.6 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$ = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.9 – 3.2 (4H, m, HCO), 2.32 (6H, t,  $J$ = 7Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.67 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.20-1.54 (72H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.9 (9H, t,  $J$  = 7.5Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 174.3 (C=O) 74.2, 72.8, 61.4 (C-O), 51.2 (OCH<sub>3</sub>) 33.8 (O=CCH<sub>2</sub>), 24.7 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.3, 29.4, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>).

#### 6.1.5.8 Ring opening of epoxidized palm oil (**2.17**) with glycerol

The experiment was conducted according to the procedure described in section 6.1.5.1. Glycerol (1.56 g, 17 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.23 g, 1.65 mmol), epoxidized palm oil (**2.17**) (5 g, 5.6 mmol), the reaction mixture polymerized 10 minutes later.  $\nu_{\text{max}}/\text{cm}^{-1}$  3295 (O-H) 2923, 2851 (C-H) 1742 (C=O) 1415 (CH<sub>2</sub>) 1033 (C-O).

#### 6.1.5.9 Ring opening of epoxidized rapeseed oil (**2.13**) with glycerol

The experiment was conducted according to the procedure described in section 6.1.5.1. Glycerol (4.14 g, 45 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.64 g, 4.5 mmol), epoxidized rapeseed oil (**2.13**) (5 g, 5.3 mmol), the reaction mixture polymerized 5 minutes later.  $\nu_{\text{max}}/\text{cm}^{-1}$  3440 (O-H) 2925, 2855 (C-H) 1738 (C=O) 1464 (CH<sub>2</sub>) 1163 (C-O) 753 (CH<sub>2</sub>).

#### 6.1.5.10 Ring opening of epoxidized soybean oil (**2.6**) with glycerol

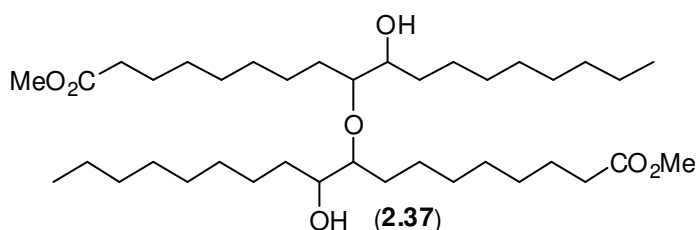
The experiment was conducted according to the procedure described in section 6.1.5.1. Glycerol (17.3 g, 0.19 mol), BF<sub>3</sub>.Et<sub>2</sub>O (2.7 g, 18.8 mmol), epoxidized



soybean oil (**2.6**) (25 g, 26.4 mmol), the reaction mixture polymerized 5 minutes later.  $\nu_{\max}/\text{cm}^{-1}$  3332 (O-H) 2924, 2855 (C-H) 1739 (C=O) 1457 (CH<sub>2</sub>) 1161, 1041 (C-O) 755 (CH<sub>2</sub>).

#### 6.1.5.11 Ring opening of epoxidized methyl oleate (**2.3**) with dihydroxy methyl stearate (**2.32**) (DHMS)

The experiment was conducted according to the procedure described in section 6.1.5.1. DHMS (7.9 g, 24 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.34 g, 2.4 mmol), epoxidized methyl oleate (**2.3**) (5 g, 16 mmol), a yellowish liquid (**2.37**, 12.5 g)  $\nu_{\max}/\text{cm}^{-1}$  3354 (O-H) 2923, 2853 (C-H) 1736 (C=O) 1458 (CH<sub>2</sub>) 1169 (C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 3.67 (6H, s, HCO), 3.60-3.25 (4H, m, HCO), 2.30 (4H, t, *J* = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.56 (4H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.55-1.20 (48H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.88 (6H, t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 174.1 (C=O) 74.3, 71.5 (C-O), 51.1 (OCH<sub>3</sub>) 33.8 (O=CCH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.2, 29.2, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.7 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 665.5327, Found 665.5327



#### 6.1.5.12 Ring opening of epoxidized cocoa butter (**2.16**) with dihydroxy methyl stearate (**2.32**) (DHMS)

The experiment was conducted according to the procedure described in section 6.1.5.1. DHMS (2.97 g, 9 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.13 g, 0.9 mmol), epoxidized cocoa

butter (**2.16**) (5 g, 6 mmol), a yellowish liquid (7.1 g);  $\nu_{\max}/\text{cm}^{-1}$  3345 (O-H) 2921, 2852 (C-H) 1740 (C=O) 1459 (CH<sub>2</sub>) 1163 (C-O) 722 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.22 (2H, m, CHO), 4.31 (2H, dd,  $J$  = 11.8 Hz, 4.0 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$  = 11.7 Hz, 5.8 Hz, CH<sub>2</sub>O), 3.67 (3H, s, HCO), 3.60-3.25 (4H, m, HCO), 2.30 (14H, t,  $J$  = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.66-1.55 (14H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.20 (176H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.9 (21H, t,  $J$  = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 174.1 (C=O) 74.3, 72.1 (C-O), 68.7 (OCH), 61.9, 61.7 (CH<sub>2</sub>O) 51.1 (OCH<sub>3</sub>) 33.8 (O=CCH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.2, 29.2, 22.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.5.13 Ring opening of epoxidized palm oil (**2.17**) with dihydroxy methyl stearate (**2.32**) (DHMS)

The experiment was conducted according to the procedure described in section 6.1.5.1. DHMS (5.45 g, 16.5 mmol), BF<sub>3</sub>.Et<sub>2</sub>O (0.23 g, 1.65 mmol), epoxidized palm oil (**2.17**) (5 g, 5.6 mmol), a yellowish liquid (**2.38**, 10.7 g);  $\nu_{\max}/\text{cm}^{-1}$  3438 (O-H) 2921, 2852 (C-H) 1736 (C=O) 1459 (CH<sub>2</sub>) 1166 (C-O) 722 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.39-5.23 (2H, m, CHO), 4.30 (2H, dd,  $J$  = 11.8 Hz, 3.6 Hz, CH<sub>2</sub>O), 4.15 (2H, dd,  $J$  = 11.7 Hz, 5.8 Hz, CH<sub>2</sub>O), 3.66 (3H, s, HCO), 3.60-3.26 (8H, m, HCO), 2.30 (18H, t,  $J$  = 7.0 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.56 (18H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.20 (144H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.87 (18H, t,  $J$  = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.7 (C=O) 74.3, 72.1 (C-O), 68.8 (OCH), 62.0, 61.8 (CH<sub>2</sub>O) 51.2 (OCH<sub>3</sub>) 33.8 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 29.1, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.1.5.14 Ring opening of epoxidized rapeseed oil (2.13) with dihydroxy methyl stearate (2.32) (DHMS)

The experiment was conducted according to the procedure described in section 6.1.5.1. DHMS (14.9 g, 45 mmol),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.64 g, 4.5 mmol), epoxidized rapeseed oil (**2.13**) (5 g, 5.3 mmol), a yellowish liquid (18.7 g),  $\nu_{\text{max}}/\text{cm}^{-1}$  3440 (O-H) 2922, 2853 (C-H) 1735 (C=O) 1459 ( $\text{CH}_2$ ) 1168 (C-O) 723 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m,  $\text{CHO}$ ), 4.31 (2H, dd,  $J$  = 11.6 Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.15 (2H, dd,  $J$  = 11.7 Hz, 5.7 Hz,  $\text{CH}_2\text{O}$ ), 3.64 (3H, s,  $\text{HCO}$ ), 3.62-3.20 (4H, m,  $\text{HCO}$ ), 2.31 (8H, t,  $J$  = 7.0 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.72-1.56 (8H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.18 (92H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (12H, t,  $J$  = 6.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 174.3 (C=O) 74.4, 72.2 (C-O), 68.6 (OCH), 62.2, 61.8 ( $\text{CH}_2\text{O}$ ) 51.2 ( $\text{OCH}_3$ ) 33.8 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 31.2, 29.3, 28.9, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ ).

#### 6.1.5.15 Ring opening of epoxidized soybean oil (2.6) with dihydroxy methyl stearate (2.32) (DHMS)

The experiment was conducted according to the procedure described in section 6.1.5.1. DHMS (12.4 g, 37 mmol),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.45 g, 3.8 mmol), epoxidized soybean oil (**2.6**) (5 g, 5.2 mmol), a yellowish liquid (15.7 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3354 (O-H) 2923, 2853 (C-H) 1736 (C=O) 1458 ( $\text{CH}_2$ ) 1169 (C-O) 723 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.27-5.22 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J$  = 11.9 Hz, 3.9 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.8 Hz, 5.7 Hz,  $\text{CH}_2\text{O}$ ), 3.66 (3H, s,  $\text{HCO}$ ), 3.62-3.20 (4H, m,  $\text{HCO}$ ), 2.30 (8H, t,  $J$  = 7.0 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.55 (8H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.20 (88H, m,  $\text{CH}_2\text{CH}_2$ ), 0.86 (12H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{CH}_3$ );

$^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 174.1 (C=O) 74.3, 72.1, 61.3 (C-O), 68.7 (OCH), 62.2, 61.8 ( $\text{CH}_2\text{O}$ ) 51.1 ( $\text{OCH}_3$ ) 33.8 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.3, 28.9, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.5.16 Ring opening of epoxidized methyl oleate (2.3) with glucose

The experiment was conducted according to the procedure described in section 6.1.5.1. Glucose (4.32 g, 24 mmol), dry DMSO (10 ml),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0.34 g, 2.4 mmol), epoxidized methyl oleate (**2.3**) (5 g, 16 mmol), a white solid (4.92 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3349 (O-H) 2925, 2853 (C-H) 1740 (C=O) 1467 ( $\text{CH}_2$ ) 1168 (C-O) 721 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 3.67 (3H, s,  $\text{HCO}$ ), 3.43-3.37 (2H, m,  $\text{HCO}$ ), 2.31 (2H, t,  $J$  = 7.0 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.54 (2H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.53-1.39 (4H, m,  $\text{HOCCCH}_2$ ), 1.38-1.19 (20H, m,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.87 (3H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{CH}_3$ ),  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 174.3 (C=O) 74.2 (C-O), 51.2 ( $\text{OCH}_3$ ) 33.7 ( $\text{O}=\text{CCH}_2$ ), 33.2 ( $\text{HOCCCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.3, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ );  $m/z$  ( $\text{ES}^+$ ) [ $\text{M}+\text{Na}^+$ ] Required 353.2662, Found 353.2664; Melting point: 65-67 °C (literature<sup>118</sup> 67-68 °C).

#### 6.1.5.17 Ring opening of epoxidized cocoa butter (2.16) with glucose

The experiment was conducted according to the procedure described in section 6.1.5.1. Glucose (Glu) (1.62 g, 9 mmol), dry DMSO (5 ml),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0.13 g, 0.9 mmol), epoxidized cocoa butter (ECB) (5 g, 6 mmol), a yellowish liquid (4.1 g),  $\nu_{\text{max}}/\text{cm}^{-1}$  2916, 2850 (C-H) 1739 (C=O) 1470 ( $\text{CH}_2$ ) 1172 (C-O) 757 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.30-5.22 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.3 Hz,  $\text{CH}_2\text{O}$ ), 4.15 (2H, dd,  $J$  = 11.8 Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 3.52-3.36 (2H, m,  $\text{HCO}$ ),

2.33 (6H, t,  $J = 7.6$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.53 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.52-1.19 (76H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.6, 172.6$  (C=O) 74.1 ( $\text{HC}-\text{O}$ ), 68.8 ( $\text{HC}-\text{O}$ ), 61.9, 61.8 ( $\text{H}_2\text{C}-\text{O}$ ), 33.7 ( $\text{O}=\text{CCH}_2$ ), 24.6 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.4, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.5.18 Ring opening of epoxidized palm oil (2.17) with glucose

The experiment was conducted according to the procedure described in section 6.1.5.1. Glucose (Glu) (3.0 g, 16.8 mmol), dry DMSO (10 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.24 g, 1.7 mmol), epoxidized palm oil (**2.17**) (5 g, 5.8 mmol), a yellowish liquid (4.7 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3450 (O-H) 2921, 2852 (C-H) 1738 (C=O) 1466 ( $\text{CH}_2$ ) 1174 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.29$ -5.22 (1H, m,  $\text{CHO}$ ), 4.29 (2H, dd,  $J = 11.8$  Hz, 4.1 Hz,  $\text{CH}_2\text{O}$ ), 4.13 (2H, dd,  $J = 11.9$  Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 3.55-3.35 (2H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.55 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.54-1.19 (72H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.8, 172.8$  (C=O) 74.3, 72.4, 62.8 ( $\text{HC}-\text{O}$ ) 68.7 ( $\text{HC}-\text{O}$ ), 62.1, 61.8 ( $\text{H}_2\text{C}-\text{O}$ ), 33.8 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.4, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

#### 6.1.5.19 Ring opening of epoxidized rapeseed oil (2.13) with glucose

The experiment was conducted according to the procedure described in section 6.1.5.1. Glucose (Glu) (8.1 g, 45 mmol), dry DMSO (10 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.64 g, 4.5 mmol), a yellowish liquid (4.7 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3353 (O-H) 2924, 2854 (C-H) 1741 (C=O) 1465 ( $\text{CH}_2$ ) 1165 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.30$ -5.22 (1H, m,  $\text{CHO}$ ), 4.29 (2H, dd,  $J = 11.9$  Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J = 11.7$

Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.75–3.36 (8H, m,  $\text{HCO}$ ), 2.34 (6H, t,  $J = 7.3$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.70–1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.53–1.19 (68H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 7.6$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.6, 172.7$  ( $\text{C}=\text{O}$ ) 74.1, 72.2, 71.8 ( $\text{HC}-\text{O}$ ) 68.7 ( $\text{HC}-\text{O}$ ), 62.0, 61.7 ( $\text{H}_2\text{C}-\text{O}$ ), 33.7 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 31.1, 29.3, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ ).

#### 6.1.5.19 Ring opening of epoxidized soybean oil (2.6) with glucose

The experiment was conducted according to the procedure described in section 6.1.5.1. Glucose (Glu) (6.75 g, 37.5 mmol), dry DMSO (10 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.53 g, 3.75 mmol), epoxidized soybean oil (**2.6**) (5 g, 5.7 mmol), a yellowish liquid (4.5 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3440 (O-H) 2924, 2855 (C-H) 1740 ( $\text{C}=\text{O}$ ) 1464 ( $\text{CH}_2$ ) 1162 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.30\text{--}5.20$  (1H, m,  $\text{CHO}$ ), 4.29 (2H, dd,  $J = 11.9$  Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J = 11.7$  Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 3.80–3.20 (10H, m,  $\text{HCO}$ ), 2.32 (6H, t,  $J = 7.0$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.72–1.55 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.45–1.15 (64, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 7.5$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.1, 172.6$  ( $\text{C}=\text{O}$ ) 74.1, 73.0, 71.8 ( $\text{HC}-\text{O}$ ) 68.7 ( $\text{HC}-\text{O}$ ), 61.9, 61.7 ( $\text{H}_2\text{C}-\text{O}$ ), 33.6 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.3, 25.5, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{CH}_2\text{CH}_3$ )

## 6.1.6 General Procedure for Ring Opening of Epoxidized Plant Oil with Water

### 6.1.6.1 Ring opening of epoxidized palm oil (2.17) by water

Epoxidized palm oil (**2.13**) (50 g, 56 mmol) was weighed into a round bottom flask. Deionized water (500 ml) and *para*-toluene sulfonic acid (21.5 g, 113 mmol) were added to (**2.13**). The mixture was stirred and heated to 100 °C for 7 hours. The reaction mixture was poured into a separating funnel and was washed with NaCl solution (100 ml), NaHCO<sub>3</sub> (100 ml) and NaCl (100 ml). The aqueous layer was discarded and CHCl<sub>3</sub> (100 ml) was added to the organic layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and CHCl<sub>3</sub> was removed *in vacuo* to yield a yellowish liquid (**2.39**, 51.6 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2922, 2853 (C-H) 1742 (C=O) 1464 (CH<sub>2</sub>) 1164 (C-O) 722 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.22 (1H, m, CHO), 4.30 (2H, dd, *J* = 11.8 Hz, 3.8 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.9 Hz, 5.7 Hz, CH<sub>2</sub>O), 3.80-3.20 (4H, m, HCO), 2.30 (6H, t, *J* = 6.5 Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 1.69-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.51-1.44 (8H, m, CH<sub>2</sub>COH) 1.43-1.20 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t, *J* = 6.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.3, 172.8 (C=O) 74.3, 72.3, 62.9 (C-O), 68.7 (OCH), 62.1, 61.8 (CH<sub>2</sub>O), 33.8 (O=CCH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.3, 29.4, 29.5, 25.1, 22.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>).

### 6.1.6.2 Ring opening of epoxidized soybean oil (2.6) by water

The experiment was conducted according to the procedure described in section 6.1.6.1. Epoxidized soybean oil (**2.6**) (5 g, 5 mmol), deionized water (15 ml), phosphoric acid (1 g, 10 mmol), a yellowish liquid (**2.40**, 5.4 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3358 (O-H) 2923, 2853 (C-H) 1743 (C=O) 1459 (CH<sub>2</sub>) 1170 (C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m, CHO), 4.30 (2H, dd, *J* = 11.9 Hz, 4.0 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.5 Hz, 5.7 Hz, CH<sub>2</sub>O), 3.80-3.20 (10H, m, HCO), 2.31

(6H, t,  $J = 6.5$  Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.70-1.55 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.52-1.44 (14H, m,  $\text{CH}_2\text{COH}$ ) 1.43-1.20 (50H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 6.5$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.2, 172.8$  (C=O) 74.2, 72.5, 65.9 (C-O), 68.7 (OCH), 62.0, 61.8 ( $\text{CH}_2\text{O}$ ), 33.8 ( $\text{O}=\text{CCH}_2$ ), 24.6 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 31.3, 29.4, 29.2, 25.0, 22.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ ).

## 6.2 GENERAL PROCEDURES FOR SUBSTRATES SYNTHESIZED IN CHAPTER 3

### 6.2.1 General procedure for polyurethanes synthesized with oligomeric polyols

#### Polyurethane (3.3) based on oligomeric polyol (2.24) as an example

Oligomeric polyol (2.24) (1 g, hydroxyl value = 35.7 mg KOH/g sample) was weighed into a round bottom flask and chloroform (2 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (0.07 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (3.3) was cured at 60 °C for 24 hours in an oven.  $\nu_{\text{max}}/\text{cm}^{-1}$  2916, 2849 (C-H) 1725 (C=O) 1530 (aromatic =CH) 1173 (C-O) 721 ( $\text{CH}_2$ );



### **6.2.2 General procedure for polyurethanes synthesized with oligomeric polyols and 1,4-butanediol**

#### **Polyurethane based on oligomeric polyol (2.24) as an example**

Oligomeric polyol (**2.24**) (1 g, hydroxyl value = 35.7 mg KOH/g sample) and 1,4-butanediol (92 mg) were weighed into a round bottom flask and chloroform (7 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (0.33 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane was cured at 60 °C for 24 hours in an oven.  $\nu_{\max}/\text{cm}^{-1}$  2915, 2849 (C-H) 1726 (C=O) 1527 (aromatic =CH) 1095 (C-O) 721 (CH<sub>2</sub>);

### **6.2.3 General procedure for polyurethanes synthesized with oligomeric polyols and polyethylene glycol**

#### **Polyurethane (3.10) based on oligomeric polyol (2.24) as an example**

Oligomeric polyol (**2.24**) (5 g, hydroxyl value = 35.7 mg KOH/g sample) and polyethylene glycol (average molecule weight = 3350) (6.5 g) were weighed into a round bottom flask and chloroform (25 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (1.7 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the

chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (**3.10**) was cured at 60 °C for 24 hours in an oven.  $\nu_{\text{max}}/\text{cm}^{-1}$  2922, 2853 (C-H) 1743 (C=O) 1597 (aromatic =CH) 1095 (C-O) 721 (CH<sub>2</sub>);

#### **6.2.4 General procedure for polyurethanes synthesized with oligomeric polyols, glycerol and polyethylene glycol**

##### **Polyurethane (**3.18**) based on oligomeric polyol (**2.23**) as an example**

Oligomeric polyol (**2.23**) (7 g, hydroxyl value = 31 mg KOH/g sample), polyethylene glycol (average molecule weight = 3350) (6.5 g) and glycerol (0.42 g) were weighed into a round bottom flask and chloroform (70 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (3.6 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (**3.18**) was cured at 60 °C for 24 hours in an oven.  $\nu_{\text{max}}/\text{cm}^{-1}$  2916, 2850 (C-H) 1734 (C=O) 1597 (aromatic =CH) 1014 (C-O) 793 (CH<sub>2</sub>);

### 6.3 General Procedures for Substrates Synthesized in Chapter 4

#### 6.3.1.1 General procedure for copolymerization of epoxidized plant oils with tetrahydrofuran [epoxidized cocoa butter (**2.16**) as an example]

Epoxidized cocoa butter (**2.16**) (50 g, 57 mmol) was weighed into a round bottom flask and dry tetrahydrofuran (250 ml) was added to it. The reactants mixture was stirred and heated at 20 °C under N<sub>2</sub> atmosphere for 30 minutes. Then BF<sub>3</sub>.Et<sub>2</sub>O (0.81 g, 5.7 mmol) was added drop-wise to the epoxidized cocoa butter (**2.16**) / tetrahydrofuran mixture. After the addition of BF<sub>3</sub>.Et<sub>2</sub>O was completed, the reaction temperature was maintained at 20 °C under N<sub>2</sub> atmosphere for another 24 hours. Then, the reaction mixture was poured into separation funnel and then saturated NaCl solution (200 cm<sup>3</sup>) and chloroform (300 cm<sup>3</sup>) were added to the reaction mixture. The aqueous layer was separated from the organic layer and the organic layer was neutralized with saturated sodium hydrogen carbonate solution (100 cm<sup>3</sup>). The organic layer was again washed with NaCl solution (200 cm<sup>3</sup>). The organic layer was dried over anhydrous MgSO<sub>4</sub> followed by removal of solvent *in vacuo* to yield a clear viscous liquid (**4.7**) (120 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3360 (O-H) 2921, 2850 (C-H) 1742 (C=O) 1105 (C-O) 754 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.24-5.28 (1H, m, CHO) 4.25 (2H, dd, *J*= 11.9 Hz, 4.4Hz, CH<sub>2</sub>O), 4.10 (2H, dd, *J*= 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.43 – 3.30 (64H, m, HCO), 2.26 (6H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.62-1.50 (72H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 1.30-1.18 (72H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.83 (9H, t, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.2, 172.8 (C=O) 70.4 (HC-O) 68.9 (HC-O), 62.0, 61.8 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 26.3 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 29.5, 22.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

### 6.3.1.2 Copolymerization of epoxidized methyl oleate (2.3) with tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized methyl oleate (**2.3**) (50 g, 160 mmol), dry tetrahydrofuran (1000 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (1.13 g, 8 mmol), clear viscous liquid (**4.4**) (78 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3353 (O-H) 2924, 2852 (C-H) 1739 (C=O) 1105 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 3.66$  (3H, s,  $\text{CH}_3\text{O}$ ), 3.62-3.50 (2H, m,  $\text{CHO}$ ), 3.46-3.34 (92H, m,  $\text{CH}_2\text{O}$ ), 2.29 (2H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.69-1.55 (94H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.50-1.20 (24H, m,  $\text{CH}_2\text{CH}_2$ ), 0.87 (3H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.4$  (C=O) 72.0, 70.1 ( $\text{HC-O}$ ) 50.7 ( $\text{H}_3\text{C-O}$ ), 33.4 ( $\text{O}=\text{CCH}_2$ ), 26.0 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 31.1, 29.2, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.6 ( $\text{CH}_2\text{CH}_3$ )

### 6.3.1.3 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (50 g, 56 mmol), tetrahydrofuran (2000 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.32 g, 2.3 mmol), clear viscous liquid (**4.10**) (403 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2918, 2851 (C-H) 1742 (C=O) 1103 (C-O) 746 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.27$ -5.20 (1H, m,  $\text{CHO}$ ), 4.27 (2H, dd,  $J = 11.9$  Hz, 4.1 Hz,  $\text{CH}_2\text{O}$ ), 4.12 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.45-3.32 (400H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.8$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.52 (406H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.35-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.86 (9H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.2$ , 172.8 (C=O) 70.6 ( $\text{HC-O}$ ) 68.9 ( $\text{HC-O}$ ), 62.2, 62.0 ( $\text{H}_2\text{C-O}$ ), 33.9 ( $\text{O}=\text{CCH}_2$ ), 26.3 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.6, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.4 Copolymerization of epoxidized rapeseed oil (2.13) with tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized rapeseed oil (**2.13**) (10 g, 10 mmol), tetrahydrofuran (1000 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.13 g, 0.9 mmol), clear viscous liquid (**4.12**) (80 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3353 (O-H) 2922, 2854 (C-H) 1740 (C=O) 1106 (C-O) 755 ( $\text{CH}_2$ ),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} =$  5.8-5.22 (1H, m,  $\text{CH}_2\text{O}$ ), 4.29 (2H, dd,  $J = 11.8$  Hz, 4.2 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.48-3.33 (400H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.4$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.54 (406H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.53-1.39 (12H, m,  $\text{CHOCH}_2\text{CH}_2$ ), 1.38-1.22 (54H, m,  $\text{CH}_2\text{CH}_2$ ), 0.87 (9H, t,  $J = 6.4$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} =$  173.0, 172.6 (C=O) 70.4 ( $\text{HC}-\text{O}$ ) 68.9 ( $\text{HC}-\text{O}$ ), 62.3, 62.1 ( $\text{H}_2\text{C}-\text{O}$ ), 33.8 ( $\text{O}=\text{CCH}_2$ ), 26.3 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.5, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.5 Copolymerization of epoxidized soybean oil (2.6) with tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized soybean oil (**2.6**) (10 g, 10 mmol), tetrahydrofuran (800 ml),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.14 g, 1 mmol) clear viscous liquid (**4.15**) (85 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3355 (O-H) 2940, 2858 (C-H) 1742 (C=O) 1105 (C-O) 746 ( $\text{CH}_2$ ),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} =$  5.28-5.22 (1H, m,  $\text{CH}_2\text{O}$ ), 4.30 (2H, dd,  $J = 11.7$  Hz, 3.2 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.46-3.35 (244H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.4$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.56 (250H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.53-1.39 (10H, m,  $\text{CHOCH}_2\text{CH}_2$ ), 1.40-1.24 (46H, m,  $\text{CH}_2\text{CH}_2$ ), 0.89 (9H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} =$  173.3, 172.9 (C=O) 70.3 ( $\text{HC}-\text{O}$ ) 68.8 ( $\text{HC}-\text{O}$ ),

61.9, 61.6 ( $\text{H}_2\text{C}-\text{O}$ ), 33.6 ( $\text{O}=\text{CCH}_2$ ), 26.2 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.3, 22.4 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.6 Copolymerization of euphorbia oil (2.18) with tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Euphorbia oil (**2.18**) (50 g, 55 mmol), tetrahydrofuran (1500 ml),  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (0.31 g, 2.2 mmol) clear viscous liquid (**4.18**) (175 g),  $\nu_{\text{max}}/\text{cm}^{-1}$  3350 (O-H) 2941, 2861 (C-H) 1744 (C=O) 1107 (C-O) 745 ( $\text{CH}_2$ ),  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.56\text{--}5.30$  (6H, m,  $\text{CH}=\text{CH}$ ), 5.28–5.23 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J = 11.9$  Hz, 4.0 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.48–3.35 (254H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 2.09–1.97 (12H, m,  $\text{CH}_2\text{CH}=\text{CH}$ ) 1.68–1.56 (260H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.52–1.23 (48H, m,  $\text{CH}_2\text{CH}_2$ ), 0.89 (9H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.0$ , 172.6 (C=O) 129.6, 125.3 ( $\text{HC}=\text{CH}$ ), 70.4 ( $\text{HC}-\text{O}$ ) 68.6 ( $\text{HC}-\text{O}$ ), 62.1, 61.7 ( $\text{H}_2\text{C}-\text{O}$ ), 33.7 ( $\text{O}=\text{CCH}_2$ ), 26.3 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.1, ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.7 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by $\text{AlCl}_3$

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (10 g, 11 mmol), dry tetrahydrofuran (200 ml),  $\text{AlCl}_3$  (0.29 g, 2.2 mmol), yellowish liquid (6 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3560 (O-H) 2924, 2854 (C-H) 1742 (C=O) 1163 (C-O) 723 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.25\text{--}5.20$  (1H, m,  $\text{CHO}$ ), 4.27 (2H, dd,  $J = 11.9$  Hz, 4.3 Hz,  $\text{CH}_2\text{O}$ ), 4.11 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.65–3.35 (4H, m,  $\text{HCO}$ ), 2.29 (6H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.64–1.54 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.36–1.19 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.86 (9H, t,  $J = 7.0$

Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.1, 172.7 (C=O) 73.3, 70.6 (HC-O), 68.7 (HC-O), 62.0, 61.8 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 24.7 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.3, 22.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.8 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by FeCl<sub>3</sub>

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), FeCl<sub>3</sub> (0.35 g, 2.2 mmol) yellowish liquid (25 g) ν<sub>max</sub>/cm<sup>-1</sup> 3351 (O-H) 2934, 2853 (C-H) 1743 (C=O) 1104 (C-O) 725 (CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.25-5.15 (1H, m, CHO), 4.31 (2H, dd, *J* = 11.7 Hz, 4.3 Hz, CH<sub>2</sub>O), 4.13 (2H, dd, *J* = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.60-3.10 (180H, m, HCO), 2.28 (6H, t, *J* = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.75-1.40 (186H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 1.35-1.15 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.3, 172.9 (C=O) 70.5 (HC-O) 68.9 (HC-O), 62.2, 61.8 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 26.3 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 29.2, 22.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.9 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by SnCl<sub>4</sub>

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), SnCl<sub>4</sub> (0.58 g, 2.3 mmol) yellowish liquid (43 g) ν<sub>max</sub>/cm<sup>-1</sup> 3336 (O-H) 2919, 2852 (C-H) 1741 (C=O) 1107 (C-O) 746 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.28-5.23 (1H, m, CHO), 4.29 (2H, dd, *J* = 11.8 Hz, 4.2Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.9 Hz,

5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.47-3.35 (252H, m,  $\text{HCO}$ ), 2.30 (6H, t,  $J = 7.4$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.57 (258H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.40-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J = 6.8$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 172.9$ , 172.4 ( $\text{C}=\text{O}$ ) 70.6 ( $\text{HC}-\text{O}$ ) 68.9 ( $\text{HC}-\text{O}$ ), 62.3, 61.9 ( $\text{H}_2\text{C}-\text{O}$ ), 33.9 ( $\text{O}=\text{CCH}_2$ ), 26.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.5, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.10 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by $\text{TiCl}_4$

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (10 g, 11 mmol), dry tetrahydrofuran (200 ml),  $\text{TiCl}_4$  (0.29 g, 2.2 mmol), yellowish liquid (10 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3563 (O-H) 2927, 2855 (C-H) 1741 ( $\text{C}=\text{O}$ ) 1162 (C-O) 724 ( $\text{CH}_2$ )  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 5.29$ -5.22 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J = 11.9$  Hz, 4.2 Hz,  $\text{CH}_2\text{O}$ ), 4.13 (2H, dd,  $J = 11.9$  Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.74-3.37 (4H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J = 7.5$  Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.55 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.54-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.89 (9H, t,  $J = 7.0$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 173.3$ , 172.9 ( $\text{C}=\text{O}$ ) 73.4, 72.3, 70.7 ( $\text{HC}-\text{O}$ ), 68.8 ( $\text{HC}-\text{O}$ ), 62.3, 61.9 ( $\text{H}_2\text{C}-\text{O}$ ), 33.8 ( $\text{O}=\text{CCH}_2$ ), 24.5 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 28.9, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.11 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by $\text{HBF}_4$

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (10 g, 11 mmol), dry tetrahydrofuran (200 ml),  $\text{HBF}_4$  (80 mg, 0.45 mmol) clear viscous liquid (38 g)  $\nu_{\text{max}}/\text{cm}^{-1}$  3360 (O-H) 2930, 2858 (C-H)



1740 (C=O) 1105 (C-O) 744 (CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.29-5.22 (1H, m, CH<sub>O</sub>), 4.29 (2H, dd, *J*= 11.9 Hz, 4.1 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J*= 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.45-3.32 (160H, m, HCO), 2.31 (6H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.54 (166H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 1.53-1.20 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.1, 172.7 (C=O) 70.5 (HC-O) 68.8 (HC-O), 62.1, 62.0 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>), 26.3 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>O), 29.5, 22.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.12 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by HBF<sub>4</sub> with addition of water

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (100 ml), de-ionised water (1 ml), HBF<sub>4</sub> (80 mg, 0.45 mmol) clear liquid (9 g), ν<sub>max</sub>/cm<sup>-1</sup> 3461 (O-H) 2922, 2853 (C-H) 1742 (C=O) 1160 (C-O) 722 (CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.29-5.23 (1H, m, CH<sub>O</sub>), 4.30 (2H, dd, *J*= 11.9 Hz, 4.0 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J*= 11.8 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.65-3.30 (2H, m, HCO), 3.15-2.80 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.31 (6H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.64-1.50 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.48-1.36 (4H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.35-1.15 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t, *J* = 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.1, 172.6 (C=O) 74.1, 70.4 (HC-O), 68.7 (HC-O), 62.0, 61.7 (H<sub>2</sub>C-O), 56.9 (CH<sub>2</sub>CHOCHCH<sub>2</sub>) 33.7 (O=CCH<sub>2</sub>), 28.2 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.4, 22.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.13 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by triflic acid

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), trifluoromethane sulfonic acid (0.34 g, 2.3 mmol) yellowish liquid (49 g)  $\nu_{\max}/\text{cm}^{-1}$  3460 (O-H) 2919, 2852 (C-H) 1742 (C=O) 1106 (C-O) 745 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.30-5.20 (1H, m,  $\text{CHO}$ ), 4.29 (2H, dd,  $J$  = 11.8 Hz, 4.1 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.50-3.30 (230H, m,  $\text{HCO}$ ), 2.31 (6H, t,  $J$  = 7.4 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.70-1.53 (236H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.40-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.3, 172.7 (C=O) 70.4 ( $\text{HC-O}$ ) 68.8 ( $\text{HC-O}$ ), 62.3, 61.7 ( $\text{H}_2\text{C-O}$ ), 33.7 ( $\text{O}=\text{CCH}_2$ ), 26.3 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2\text{CH}_2\text{O}$ ), 29.5, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.1.14 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by sulfuric acid

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), sulfuric acid (0.22 g, 2.2 mmol), yellowish liquid (9 g);  $\nu_{\max}/\text{cm}^{-1}$  3465 (O-H) 2922, 2853 (C-H) 1743 (C=O) 1159 (C-O) 722 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.30-5.22 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.3 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.76-3.34 (2H, m,  $\text{HCO}$ ), 3.14-2.82 (2H, m,  $\text{CH}_2\text{CHOCHCH}_2$ ), 2.31 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.55-1.44 (4H, m,  $\text{CHOCH}_2\text{CH}_2$ ), 1.43-1.19 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.89 (9H, t,  $J$  = 6.8 Hz,

CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 173.2, 172.7 (C=O) 73.6, 70.6 (HC-O), 68.7 (HC-O), 62.0, 61.8 (H<sub>2</sub>C-O), 57.0 (CH<sub>2</sub>CHOCHCH<sub>2</sub>) 33.8 (O=CCH<sub>2</sub>), 28.1 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.6 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.15 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by chlorosulfonic acid

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), chlorosulfonic acid (0.29 g, 2.2 mmol), yellowish liquid (10 g) ν<sub>max</sub>/cm<sup>-1</sup> 3563 (O-H) 2927, 2853 (C-H) 1740 (C=O) 1160 (C-O) 721 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.29-5.22 (1H, m, CH<sub>2</sub>O), 4.30 (2H, dd, *J* = 11.9 Hz, 4.0 Hz, CH<sub>2</sub>O), 4.14 (2H, dd, *J* = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.65-3.35 (2H, m, HCO), 3.15-2.85 (2H, m, CH<sub>2</sub>CHOCHCH<sub>2</sub>), 2.31 (6H, t, *J* = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.45 (4H, m, CHOCH<sub>2</sub>CH<sub>2</sub>), 1.40-1.20 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.89 (9H, t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 172.7, 172.3 (C=O) 74.2, 72.6 (HC-O), 68.9 (HC-O), 62.1, 61.7 (H<sub>2</sub>C-O), 56.6 (CH<sub>2</sub>CHOCHCH<sub>2</sub>) 34.1 (O=CCH<sub>2</sub>), 28.3 (CHOCH<sub>2</sub>CH<sub>2</sub>), 24.8 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.7, 22.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.0 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.3.1.16 Copolymerization of epoxidized palm oil (2.17) with tetrahydrofuran catalyzed by trifluoroacetic acid

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (2.17) (10 g, 11 mmol), dry tetrahydrofuran (200 ml), trifluoroacetic acid (0.25 g, 2.2 mmol) yellowish liquid (7 g) ν<sub>max</sub>/cm<sup>-1</sup> 3620 (O-H) 2923, 2853 (C-H) 1741 (C=O) 1161 (C-O) 823 (CHOCHCH<sub>2</sub>) 724 (CH<sub>2</sub>) <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.22 (1H, m,  $\text{CHO}$ ), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.2 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.73-3.41 (2H, m,  $\text{HCO}$ ), 2.95-2.73 (2H, m,  $\text{CH}_2\text{CHOCHCH}_2$ ), 2.32 (6H, t,  $J$  = 7.5 Hz,  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.67-1.57 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.56-1.50 (4H, m,  $\text{CHOCH}_2\text{CH}_2$ ), 1.49-1.24 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.89 (9H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.1, 172.7 (C=O) 73.6, 71.8 ( $\text{HC-O}$ ), 68.7 ( $\text{HC-O}$ ), 62.0, 61.8 ( $\text{H}_2\text{C-O}$ ), 57.3 ( $\text{CH}_2\text{CHOCHCH}_2$ ) 33.9 ( $\text{O}=\text{CCH}_2$ ), 27.9 ( $\text{CHOCH}_2\text{CH}_2$ ), 24.6 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.3, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{CH}_2\text{CH}_3$ )

#### 6.3.2.1 Attempted copolymerization of epoxidized palm oil (2.17) with 2-methyl tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (1 g, 1.1 mmol), 2-methyl tetrahydrofuran (20 ml), BF<sub>3</sub>.Et<sub>2</sub>O (3 mg, 0.022 mmol) yield back starting material epoxidised palm oil (**2.17**) (0.7 g).

#### 6.3.2.2 Attempted copolymerization of epoxidized palm oil with 3-methyl tetrahydrofuran

The experiment was conducted according to the procedure described in 6.3.1.1. Epoxidized palm oil (**2.17**) (0.1 g, 0.11 mmol), 3-methyl tetrahydrofuran (1 ml), BF<sub>3</sub>.Et<sub>2</sub>O (3 mg, 0.022 mmol) yield back starting material epoxidised palm oil (**2.17**) (95 mg).

### 6.3.3 Homopolymerization of tetrahydrofuran catalyzed by triflic acid

Tetrahydrofuran (THF) (150 g, 2.1 mol) was weighed into a round bottom flask and was stirred and heated at 60 °C under N<sub>2</sub> atmosphere for 30 minutes. Then triflic acid (CF<sub>3</sub>SO<sub>3</sub>H) (24.0 g, 0.16 mol) was added drop-wise to the THF. After the addition of triflic acid was completed, the reaction temperature was maintained at 60 °C under N<sub>2</sub> atmosphere for another 8 hours. Then, the reaction mixture was poured into separation funnel. Cyclohexane (300 ml) and deionized water (300 ml) were added to it. The aqueous layer was discarded and the organic layer was washed with sodium bicarbonate solution (300 ml). The organic layer was separated from the aqueous layer. The organic layer was again washed with deionized water (300 ml). The organic layer was separated from the aqueous and was dried over anhydrous MgSO<sub>4</sub>. The cyclohexane was removed *in vacuo* to yield homopolymer of THF (**4.19**) (61.4 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3462 (O-H) 2924, 2854 (C-H) 1741 (C=O) 1464 (CH<sub>2</sub>) 1088 (C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 3.43 (4H, t, *J* = 7.7 Hz, CH<sub>2</sub>O), 1.68-1.56 (4H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 70.3, (HC-O), 26.2 (CH<sub>2</sub>CH<sub>2</sub>)

### 6.3.4 Copolymerization of $\epsilon$ -caprolactone with epoxidized palm oil (**2.17**)

Epoxidized palm oil (**2.17**) (40 g, 45 mmol) and  $\epsilon$ -caprolactone (10.2, 90 mmol) were weighed into a round bottom flask and dry dichloromethane (200 ml) was added to it. The reactants mixture was stirred and heated at 20 °C under N<sub>2</sub> atmosphere for 30 minutes. Then BF<sub>3</sub>.Et<sub>2</sub>O (640 mg, 4.5 mmol) was added drop-wise to the epoxidized palm oil /  $\epsilon$ -caprolactone mixture. After the addition of BF<sub>3</sub>.Et<sub>2</sub>O was completed, the reaction temperature was maintained at 20 °C under N<sub>2</sub> atmosphere for another 24 hours. Then, the reaction mixture was poured into

separation funnel and  $\text{CHCl}_3$  (100 ml) was added to it. The organic layer was washed with sodium bicarbonate solution (50 ml). The organic layer was separated from the aqueous layer. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and  $\text{CHCl}_3$  was removed *in vacuo* to yield copolymers (**4.24**) (50 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  3475 (O-H) 2923, 2853 (C-H) 1737 (C=O) 1461 ( $\text{CH}_2$ ) 1164 (C-O) 722 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m,  $\text{CHO}$ ), 4.87-4.80 (1H, m,  $\text{CHOC=O}$ ), 4.30 (2H, dd,  $J$  = 11.8 Hz, 3.8 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.8 Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 4.06 (2H, t,  $J$  = 6.5 Hz,  $\text{O=COCH}_2$ ) 3.61 (2H, t,  $J$  = 6.4 Hz,  $\text{HOCH}_2$ ), 3.58-3.10 (4H, m,  $\text{HCO}$ ), 2.32 (8H, t,  $J$  = 7.5 Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.71-1.52 (10H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 1.53-1.39 (4H, m,  $\text{CH}_2\text{CH}_2$ ), 1.36-1.18 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J$  = 6.6 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.1, 172.6 (C=O) 76.2, 74.3, 72.0 ( $\text{HC-O}$ ), 68.7 ( $\text{HC-O}$ ), 63.7, 62.2, 61.8 ( $\text{H}_2\text{C-O}$ ), 61.9 ( $\text{H}_2\text{C-OH}$ ), 33.8 ( $\text{O=CCH}_2$ ), 24.6 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 29.4, 22.6 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ )

### 6.3.5 General Procedure for Polyurethanes Synthesized with Copolymers Polyol

#### 6.3.5.1 Polyurethane made from copolymerized epoxidized palm oil and tetrahydrofuran (**4.10**) as an example.

Copolymerized epoxidized palm oil and tetrahydrofuran (**4.10**) (10 g, hydroxyl value = 30.5 mg KOH/g sample) was weighed into a round bottom flask and chloroform (150 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (1.7 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary

evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (**4.10PU**) was cured at 60 °C for 24 hours in an oven.  $\nu_{\max}/\text{cm}^{-1}$  3308 (O=CNH) 2915, 2849 (C-H) 1729 (C=O) 1595 (aromatic =CH) 1098 (C-O) 721 (CH<sub>2</sub>)

### **6.3.6 Differential Scanning Calorimetric (DSC) and Thermogravimetric (TGA) method**

DSC and TGA of polyurethane samples were conducted in a Mettler Toledo TGA/DSC 1 system. For DSC analysis, the samples were scanned from -100 °C to 600 °C at a heating rate of 10 K per minute in the presence of nitrogen. For TGA analysis, the samples were scanned from 25 °C to 600 °C at a heating rate of 10 K per minute in the presence of nitrogen.

### **6.3.7 Tensile test method**

Tensile strength and elongation at break of polyurethane samples were determined according to EN ISO 529-4: 1997 (CEN1997a). This is the European standard test method for the determination of tensile properties of polymeric materials. Testing was conducted with an Instron 5800 universal testing machine with an initial cross-head speed of 1 mm/minute for 2 minutes and then 50 mm/minute. The test specimens were of the type 1BA.

## 6.4 General Procedures for Substrates Synthesized in Chapter 5

### 6.4.1.1 General procedure for one-pot oligomerization of unsaturated plant oil with $\text{Na}_2\text{WO}_4$

#### [Rapeseed oil (2.11) as an example]

Rapeseed oil (70 g, 80 mmol),  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (3 g, 9 mmol), Aliquat 336 (4 g, 9 mmol) and  $\text{H}_2\text{O}_2$  (30% w/w, 257 g, 2270 mmol) were charged into a 3-neck round bottom flask equipped with magnetic stirrer bar and reflux condenser. The mixture was heated to 100 °C and stirred vigorously for 8 hours. The mixture was then poured into a separating funnel and was left to cool. The aqueous layer was separated from the organic layer. The organic layer was diluted with equal amount of dichloromethane (100 ml) and neutralized with saturated  $\text{Na}_2\text{CO}_3$  (50 ml). The organic layer was again washed with NaCl solution (100 cm<sup>3</sup>). The organic layer was dried over anhydrous  $\text{MgSO}_4$  followed by removal of solvent *in vacuo* to yield a viscous pale yellow liquid (68.1 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  2926, 2856 (C-H) 1738 (C=O) 1459 (CH<sub>2</sub>) 1165 (C-O) 754 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.20 (1H, m, CHO), 4.32 (2H, dd, *J*= 11.9 Hz, 3.7 Hz, CH<sub>2</sub>O), 4.16 (2H, dd, *J*= 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.75-3.30 (4H, m, CHO), 2.34 (6H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.39-1.21 (54H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.90 (9H, t, *J*= 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.1, 172.7 (C=O), 72.2 (HC-O), 68.7 (HC-O), 62.1, 61.7 (H<sub>2</sub>C-O), 33.7 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.2, 29.2, 22.6 (CH<sub>2</sub>CH<sub>2</sub>), 24.3 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.7 (CH<sub>2</sub>CH<sub>3</sub>).



#### 6.4.1.2 One-pot oligomerization of palm oil (**2.10**) with sodium tungstate

The experiment was conducted according to the general procedure described in 6.4.1.1. Palm oil (**2.10**) (100 g, 116 mmol), Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (2.7 g, 8 mmol), Aliquat 336 (3.6 g, 8 mmol) and H<sub>2</sub>O<sub>2</sub> (30% w/w, 224 g, 1976 mmol) viscous pale yellow liquid (95.8 g).  $\nu_{\max}/\text{cm}^{-1}$  2929, 2858 (C-H) 1741 (C=O) 1461 (CH<sub>2</sub>) 1165 (C-O) 754 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.20 (1H, m, CHO), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.2 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.70-3.56 (2H, m, CHO), 2.35 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.69-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.53-1.21 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.90 (9H, t,  $J$  = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.3, 172.9 (C=O), 72.5 (HCO), 68.9 (HCO), 62.3, 61.9 (H<sub>2</sub>C-O), 33.9 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.1, 29.3, 22.5 (CH<sub>2</sub>CH<sub>2</sub>), 24.4 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>).

#### 6.4.1.3 One-pot oligomerization of soybean oil (**2.12**) with sodium tungstate

The experiment was conducted according to the general procedure described in 6.4.1.1. The experiment was conducted according to the general procedure described above. Soybean oil (**2.12**) (70 g, 80 mmol), Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (3.4 g, 10 mmol), Aliquat 336 (4 g, 9 mmol) and H<sub>2</sub>O<sub>2</sub> (30% w/w, 267 g, 2355 mmol) viscous pale yellow liquid (67.5 g).  $\nu_{\max}/\text{cm}^{-1}$  2930, 2860 (C-H) 1742 (C=O) 1455 (CH<sub>2</sub>) 1160 (C-O) 752 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.30-5.23 (1H, m, CHO), 4.30 (2H, dd,  $J$  = 11.9 Hz, 4.1 Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$  = 11.9 Hz, 5.8 Hz, CH<sub>2</sub>O), 3.80-3.30 (4H, m, CHO), 2.34 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.21 (48H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.90 (9H, t,  $J$  = 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.2, 172.8 (C=O), 72.6 (HCO), 68.8 (HCO), 62.1, 61.8 (H<sub>2</sub>C-O),

33.5 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.2, 29.5, 22.3 (CH<sub>2</sub>CH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.9 (CH<sub>2</sub>CH<sub>3</sub>).

#### 6.4.1.4 One-pot oligomerization of soybean oil (2.12) and palm oil (2.10) with sodium tungstate

The experiment was conducted according to the general procedure described in 6.4.1.1. The experiment was conducted according to the general procedure described above. Soybean oil (2.12) (50 g, 57 mmol), palm oil (2.10) (50 g, 57 mmol), Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (2.6 g, 8 mmol), Aliquat 336 (3.5 g, 8 mmol) and H<sub>2</sub>O<sub>2</sub> (30% w/w, 220 g, 1941 mmol) viscous pale yellow liquid (97.8 g).  $\nu_{\max}/\text{cm}^{-1}$  2929, 2859 (C-H) 1740 (C=O) 1460 (CH<sub>2</sub>) 1160 (C-O) 752 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.31-5.23 (1H, m, CH<sub>2</sub>O), 4.30 (2H, dd,  $J$  = 11.7 Hz, 4.1 Hz, CH<sub>2</sub>O), 4.15 (2H, dd,  $J$  = 11.8 Hz, 6.0 Hz, CH<sub>2</sub>O), 3.80-3.35 (4H, m, CH<sub>2</sub>O), 2.33 (6H, t,  $J$  = 7.6 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.53-1.21 (56H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.90 (9H, t,  $J$  = 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.1, 172.7 (C=O), 72.1 (HC-O), 68.6 (HC-O), 62.0, 61.7 (H<sub>2</sub>C-O), 33.7 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.0, 29.1, 22.2 (CH<sub>2</sub>CH<sub>2</sub>), 24.2 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>).

#### 6.4.2.1 General procedure for the oligomerization of unsaturated plant oil with tungsten powder

##### [Rapeseed oil (2.11) as an example]

Tungsten powder (12  $\mu\text{m}$ , 99.99%, 0.9 g, 4.9 mmol), hydrogen peroxide (30% w/w, 8 g, 61.8 mmol) and deionised water (3.5 cm<sup>3</sup>) were charged into a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was stirred and heated up to 50 °C until the tungsten powder was totally dissolved, then H<sub>3</sub>PO<sub>4</sub>

(85%, 0.65 g, 5.6 mmol) in water (7 cm<sup>3</sup>) was added into it (this is the tungsten catalyst solution). Rapeseed oil (170 g, 0.21 mol) and Adogen 464 (1.2 g, 3 mmol) were charged into another 3-neck round bottom flask equipped with a motor stirrer. The oil mixture was heated to the desired temperature and stirred vigorously. The tungsten catalyst solution was added to the oil mixture followed by water (300 cm<sup>3</sup>), hydrogen peroxide (115 g, 0.97 mol) and H<sub>3</sub>PO<sub>4</sub> (101.1 g, 0.877 mol). The temperature of the oil mixture was kept at 100 °C for 8 hours. The oil mixture was then poured into a separating funnel, and then saturated NaCl solution (100 cm<sup>3</sup>) and dichloromethane (100 cm<sup>3</sup>) were added to the oil mixture. The aqueous layer was separated from the organic layer. The organic layer was neutralized with saturated sodium hydrogen carbonate solution (100 cm<sup>3</sup>). The organic layer was again washed with NaCl solution (100 cm<sup>3</sup>). The organic layer was dried over anhydrous MgSO<sub>4</sub> followed by removal of solvent *in vacuo* to yield a viscous pale yellow liquid (165 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  2924, 2854 (C-H) 1740 (C=O) 1460 (CH<sub>2</sub>) 1164 (C-O) 752 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m, CHO), 4.27 (2H, dd,  $J$ = 11.9 Hz, 4.4Hz, CH<sub>2</sub>O), 4.14 (2H, dd,  $J$ = 11.6 Hz, 5.8 Hz, CH<sub>2</sub>O), 3.60-3.40 (1H, m, CHO), 2.36 (6H, t,  $J$ = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.38-1.20 (54H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.92 (9H, t,  $J$ = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 173.3, 172.9 (C=O), 74.3 (HC-O), 68.8 (HC-O), 62.1, 61.8 (H<sub>2</sub>C-O), 33.8 (O=CCH<sub>2</sub>CH<sub>2</sub>), 31.3, 28.9, 22.5 (CH<sub>2</sub>CH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>).

#### 6.4.2.2 One-pot oligomerization of soybean oil (2.12) and palm oil (2.10) with tungsten powder

The experiment was conducted according to the general procedure described in 6.4.2.1. Tungsten powder (12  $\mu\text{m}$ , 99.99%, 0.3 g, 1.6 mmol), hydrogen peroxide (30% w/w, 43 g, 380 mmol), deionised water (101.5 g),  $\text{H}_3\text{PO}_4$  (85%, 28 g, 0.3 mol), soybean oil (50 g, 57 mmol), palm oil (50 g, 57 mmol), Adogen 464 (0.4 g, 1 mmol), a viscous pale yellow liquid (97.3 g).  $\nu_{\text{max}}/\text{cm}^{-1}$  2920, 2850 (C-H) 1740 (C=O) 1465 ( $\text{CH}_2$ ) 1168 (C-O) 751 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.29-5.21 (1H, m,  $\text{CH=O}$ ), 4.29 (2H, dd,  $J$  = 11.9 Hz, 4.3 Hz,  $\text{CH}_2\text{O}$ ), 4.14 (2H, dd,  $J$  = 11.8 Hz, 5.9 Hz,  $\text{CH}_2\text{O}$ ), 3.76-3.33 (2H, m,  $\text{CH=O}$ ), 2.31 (6H, t,  $J$  = 7.5 Hz,  $\text{O=CCH}_2\text{CH}_2$ ), 1.67-1.54 (6H, m,  $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 1.53-1.21 (54H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J$  = 6.8 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 173.5, 172.8 ( $\text{C=O}$ ), 73.5 ( $\text{HC-O}$ ), 68.8 ( $\text{HC-O}$ ), 62.1, 61.9 ( $\text{H}_2\text{C-O}$ ), 33.8 ( $\text{O=CCH}_2\text{CH}_2$ ), 31.0, 29.5, 22.3 ( $\text{CH}_2\text{CH}_2$ ), 24.6 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 13.8 ( $\text{CH}_2\text{CH}_3$ ).

#### 6.4.3 Synthesis of oleic acid based oligomers (5.6)

Oleic acid (5.5) (100 g, 0.354 mol),  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (2.5 g, 7.5 mmol), Aliquat 336 (3.4 g, 7.7 mmol),  $\text{H}_2\text{O}_2$  (30% w/w, 215 g, 1.9 mol) were charged into a 3-neck round bottom flask equipped with magnetic stirrer bar and reflux condenser. The mixture was heated to 100  $^\circ\text{C}$  and stirred vigorously for 24 hours. The mixture was then poured into a separating funnel and was left to cool. The mixture separated into an organic and aqueous layer, with some white precipitate in the aqueous layer. The aqueous layer together with the white precipitate was separated from the organic layer. The white precipitate was filtered from the aqueous and washed with deionised water (3 x 100 ml) to remove any aqueous residual. Then it was dried in oven and

was characterized to be 1,9-nonanedioic acid (azelaic acid) (1.5 g, 7.98 mmol, 2.3%) (**5.14**).  $\nu_{\text{max}}/\text{cm}^{-1}$  1695 (C=O) 2932, 2856 (C-H) 1684 (C=O) 1468 (CH<sub>2</sub>) 1251 (C-O) 912 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta_{\text{H}}$  = 12.0 (2H, s, COOH), 2.20 (4H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.46-1.53 (4H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.08-1.40 (6H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) <sup>13</sup>C NMR (100 MHz DMSO-d<sub>6</sub>):  $\delta_{\text{C}}$  = 174.4 (C=O), 34.0 (O=CCH<sub>2</sub>), 28.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 24.4 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 211.0941, Found 211.0941; melting point = 106 - 108 °C ( literature<sup>113</sup>: 105 – 107 °C) [Found: C, 58.0; H, 8.7; C<sub>9</sub>H<sub>16</sub>O<sub>4</sub>, Required C, 57.4; H, 8.6; O, 34].

The organic layer was diluted with equal amount of dichloromethane (100 ml) and dried over MgSO<sub>4</sub>. It was filtered and the solvent removed *in vacuo* to yield crude product (**5.6**) (95 g) as a viscous pale yellow liquid. A small amount of (**5.6**) (250 mg) was purified by column chromatography  $R_f$  0.3 (petroleum ether (40-60°C)/ethyl acetate, 8:2) to yield purified (**5.6**) (190 mg, 0.157 mmol, 64%) as a viscous liquid.  $\nu_{\text{max}}/\text{cm}^{-1}$  3354 (O-H), 2924, 2854 (C-H) 1708 (C=O) 1175 (C-O); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 4.86-4.80 (2H, m, HCOC=O), 3.61-3.56 (2H, m, HCO) 3.44-3.39 (2H, m, HCO), 2.33 (6H, t,  $J$  = 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.55 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.51-1.21 (72H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.9 (9H, t,  $J$  = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 179.7 (C=O), 77.4, 77.6, 72.7 (C-O), 34.0 (O=CCH<sub>2</sub>), 29.2 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 33.0, 29.2, 29.0, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 15.0 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>) [M+Na<sup>+</sup>] Required 935.7527, Found 935.7522

#### 6.4.4 Saponification of estolides (5.6)

2.5 g (2.06 mmol) of (5.6) was dissolved in 20 ml tetrahydrofuran in a 100 ml round bottom flask equipped with a magnetic stirrer. Then 1.3 g (32.5 mmol) of sodium hydroxide was dissolved in 20 ml deionised water and this sodium hydroxide solution was added to the round bottom flask. The mixture was heated to 80 °C for 12 hour under reflux, which was then acidify to pH=1 with 2 M HCl. The reaction mixture was poured into a separating funnel and the aqueous layer was separated from the organic layer. The aqueous layer was extracted with CHCl<sub>3</sub> (100 ml) and the CHCl<sub>3</sub> was combined with the organic layer, which was dried over MgSO<sub>4</sub>. The organic layer was filtered and the solvent removed *in vacuo* to yield crude product (2.05 g). A small amount of crude product (250 mg) was purified by column chromatography (petroleum ether (40-60°C)/ethyl acetate, 7:3) to yield purified (5.11) (182 mg, 0.576 mmol, 57%) as a white solid.  $R_f$  0.3 (petroleum ether (40-60°C)/ethyl acetate, 7:3);  $\nu_{\max}/\text{cm}^{-1}$  3292 (O-H) 2915, 2847 (C-H) 1716 (C=O) 1467 (CH<sub>2</sub>) 1076 (C-O) 719(CH<sub>2</sub>) <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta_H$  = 12.0 (1H, s, COOH), 3.24-3.18 (2H, m, HCOH), 2.2 (2H, t,  $J$ = 7.5 Hz, O=CCH<sub>2</sub>), 1.65-1.55 (2H, m, HOOCCH<sub>2</sub>CH<sub>2</sub>), 1.50-1.35 (2H, m, HOCHCH<sub>2</sub>), 1.35-1.20 (20H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.85 (3H, t,  $J$ = 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz DMSO-d<sub>6</sub>):  $\delta_C$  = 174.5 (C=O), 73.1 (C-OH), 33.6 (O=CCH<sub>2</sub>), 31.3 (HOCHCH<sub>2</sub>), 24.3 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.1, 28.0, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>),  $m/z$  (ES<sup>+</sup>), [M+Na<sup>+</sup>] Required 339.2511, Found 339.2506; melting point = 95 - 96 °C (literature<sup>114</sup>: 94 °C) [Found: C, 68.3; H, 11.5; C<sub>18</sub>H<sub>36</sub>O<sub>4</sub> Required C, 68.3; H, 11.5; O, 20.2].

#### 6.4.5 Reduction of estolides (5.6)

2.5g (2.06 mmol) of (**5.6**) was dissolved in 25 ml dry tetrahydrofuran in a 100 ml round bottom flask equipped with a magnetic stirrer under nitrogen gas atmosphere. The reactant was cooled to 0 °C with an ice bath. Then, 40 ml of LiAlH<sub>4</sub> (1M, 40 mmol) was slowly added to the reactant while the reactant was being stirred. After the addition has finished, the reaction temperature was raised to room temperature and held for 24 hours. After 24 hours, the excess LiAlH<sub>4</sub> was decomposed with deionised water and 20 ml of H<sub>2</sub>SO<sub>4</sub> (10% concentration) was added to reactant mixture. The reaction mixture was poured into separating funnel and the aqueous layer was separated from the organic layer. The aqueous layer was extracted with CHCl<sub>3</sub> (2 x 100 ml) and the CHCl<sub>3</sub> was combined with the organic layer, which was dried over MgSO<sub>4</sub>. The organic layer was filtered and the solvent removed *in vacuo* to yield crude product (1.63 g). A small amount of crude product (250 mg) was purified by column chromatography (petroleum ether (40-60°C)/ethyl acetate, 8:2) to yield purified (**5.12**) (175 mg, 0.58 mmol, 46%) as a white solid. R<sub>f</sub> 0.3 (petroleum ether (40-60°C)/ethyl acetate, 8:2);  $\nu_{\max}/\text{cm}^{-1}$  3340 (O-H) 2915, 2847 (C-H) 1463 (CH<sub>2</sub>) 1057(C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 3.60 (2H, t, *J*= 6.6 Hz, HCOH), 3.43-3.38 (2H, m, HCOH), 1.64-1.51 (2H, m, HOCCH<sub>2</sub>), 1.50-1.42 (2H, m, HOCCH<sub>2</sub>) 1.40-1.20 (22H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.87 (3H, t, *J*= 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 72.7, 62.4 (C-OH), 33.0 (HOCHCH<sub>2</sub>), 29.2 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.0, 28.7, 25.1, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 15.0 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* (ES<sup>+</sup>), [M+Na<sup>+</sup>] Required 325.2713, Found 325.2714; melting point = 70 - 82 °C (literature<sup>115</sup>: 82 °C) [Found: C, 71.3; H, 12.4; C<sub>18</sub>H<sub>36</sub>O<sub>4</sub> requires C, 71.5; H, 12.7; O, 15.9].

#### 6.4.6 Synthesis of 9,10-dihydroxystearic acid (**5.11**) from oleic acid

Oleic acid (**5.5**) (250 g, 708 mmol), H<sub>2</sub>O<sub>2</sub> (10 g, 88 mmol), H<sub>2</sub>SO<sub>4</sub> (0.6 g, 6 mmol) and HCOOH (41.4 g, 900 mmol) were weighed into a 3-neck round bottom flask. The mixture was stirred without heating as this is an exothermic reaction and when the temperature of the mixture reaches 40 °C, another portion of H<sub>2</sub>O<sub>2</sub> (80 g, 706 mmol) was added drop-wise to the mixture while maintaining the reaction temperature at 60 °C. Once the addition of H<sub>2</sub>O<sub>2</sub> was completed, the reaction temperature was raised and maintained at 90 °C for 24 hour. Then, the reaction mixture was poured into separating funnel and the organic layer was separated from the aqueous layer. Then 150 ml of NaOH solution (50% concentration) was added to the organic layer and the mixture was heated to 100 °C under reflux for 8 hour. Then the mixture was acidify to pH=1 with 2 M HCl and poured into separating funnel, where the organic layer was separated from the aqueous layer. The organic layer was dissolved in hot n-hexane at 60 °C and was left to recrystallize overnight. The white precipitate was filtered and washed with n-hexane to yield about 140 g of (**5.11**) (440 mmol, 62% yield).

#### 6.4.7 Synthesis of diacetate estolides (**5.17**)

The compound (**5.11**) (31.6 g, 100 mmol), acetic anhydride (31 g, 304 mmol) and H<sub>3</sub>PO<sub>4</sub> (1 g, 10 mmol) were weighed into a round bottom flask and was heated to 100 °C for 6 hour. Then, the mixture was poured into separating funnel and 100 ml of CHCl<sub>3</sub> was added to the mixture. The organic layer was separated from the aqueous layer and the aqueous layer was again extracted with 100 ml of CHCl<sub>3</sub>. The organic layer was combined, dried over MgSO<sub>4</sub> and was filtered. The solvent was removed *in vacuo* to yield (**5.17**) (26.7 g, 360 mmol, 36% yield).  $\nu_{\max}/\text{cm}^{-1}$  2925, 2855 (C-H)



1737, 1710 (C=O) 1465 (CH<sub>2</sub>) 1371 (O=CCH<sub>3</sub>) 1225 (C-O-C) 1022 (C-O) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.03-4.96 (4H, m, HCOC=O), 2.43 (2H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 2.33 (2H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 2.06 (9H, s, O=CCH<sub>3</sub>), 1.69-1.57 (4H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.56-1.47 (8H, m, OCHCH<sub>2</sub>), 1.38-1.18 (40H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.87 (6H, t, *J*= 6.8 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 179.3, 173.3, 170.6 (C=O) 73.2, 72.9 (C-O), 35.1, 34.2 (O=CCH<sub>2</sub>), 29.1 (CH<sub>2</sub>CHO), 24.1 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 22.6 (O=CCH<sub>3</sub>), 28.6, 24.1, 22.6, 20.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.1 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* (ES<sup>+</sup>), [M+Na<sup>+</sup>] Required 763.5336, Found 763.5333.

#### 6.4.8 Synthesis of 9,10-dimethoxy methyl stearate (5.18)

Potassium hydroxide (KOH) (20 g, 357 mmol) was grounded to powder and was charged into a round bottom flask. Then, 9,10-dihydroxy methyl stearate (**5.9**) (30 g, 91 mmol) and anhydrous tetrahydrofuran (50 ml) were added to this mixture with stirring and the temperature was maintained at 40 °C for another an hour. Thereafter, methyl iodide (50 g, 350 mmol) was added drop-wise to the mixture and the reaction temperature was maintained at 40 °C for 24 hour. Then, the mixture was poured into separating funnel. 200 ml of NaCl solution and 300 ml of CHCl<sub>3</sub> was added to the mixture. The organic layer was separated from the aqueous layer and the aqueous layer was again extracted with 300 ml of CHCl<sub>3</sub>. The organic layer was combined, dried over MgSO<sub>4</sub> and was filtered. The solvent was removed *in vacuo* to yield (**5.18**) as a pale yellow oil (16.3 g, 45.5 mmol, 50% yield). *v*<sub>max</sub>/cm<sup>-1</sup> 2922, 2853 (C-H) 1741 (C=O) 1455 (CH<sub>2</sub>) 1094 (C-O) 722 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 3.63 (3H, s, HCO), 3.40 (6H, s, HCO), 3.30-3.20 (2H, m, HCO) 2.30 (2H, t, *J*= 7.5 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>), 1.60-1.50 (2H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.50-1.40 (4H, m, MeOCCH<sub>2</sub>), 1.35-1.25 (22H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.88 (3H, t, *J*= 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C

NMR (100 MHz CDCl<sub>3</sub>):  $\delta_C$  = 174.1 (C=O) 81.9 (HC-OMe), 57.1 (OCH<sub>3</sub>) 49.5 (O=COCH<sub>3</sub>) 39.1 (O=CCH<sub>2</sub>), 30.3 (CH<sub>2</sub>CHO), 27.1 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 26.6, 23.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 14.5 (CH<sub>2</sub>CH<sub>3</sub>);  $m/z$  (ES<sup>+</sup>), [M+Na<sup>+</sup>] Required 381.2981, Found 381.2975.

#### **6.4.9 General procedure for oxidative cleavage of fatty acid derivatives**

##### **6.4.9.1 Oxidative cleavage of epoxidized methyl oleate (5.16) as an example**

Epoxidised methyl oleate (**5.16**) (50 g, 160 mmol), Na<sub>2</sub>WO<sub>4</sub> (1.25 g, 3.79 mmol), Aliquat 336 (1.7 g, 3.85 mmol) and H<sub>2</sub>O<sub>2</sub> (30% w/v) (100 g, 880 mmol) were weighed into a round bottom flask and the reaction mixture was stirred and heated to 100 °C for 24 hour. After 24 hour, 100 ml deionised water and 4 g H<sub>3</sub>PO<sub>4</sub> were added to the reaction mixture. The reaction mixture was stirred and heated at 100 °C for another 24 hour. The reaction mixture was poured into separating funnel after 24 hour of reaction and 100 ml of NaCl solution was added to the separating funnel, then the mixture was left overnight for any azelaic acid to precipitate from the aqueous layer. The precipitated azelaic acid (**5.14**) in the aqueous layer was filtered and washed with deionised water, then dried overnight in oven. The weight of (**5.14**) collected is 0.92 g (4.9 mmol, 3% yield)

##### **6.4.9.2 Oxidative cleavage of 9,10-dihydroxystearic acid (5.11)**

The experiment was conducted according to the procedure described in 6.4.9.1. The compound (**5.11**) (12 g, 38 mmol), Na<sub>2</sub>WO<sub>4</sub> (0.22 g, 0.68 mmol), Aliquat 336 (0.3 g, 0.68 mmol) and H<sub>2</sub>O<sub>2</sub> (30% w/v) (19.3 g, 170 mmol). The weight of azelaic acid (**5.14**) collected is 70 mg (0.37 mmol, 0.98% yield).

#### 6.4.9.3 Oxidative cleavage of diacetate estolides (5.17)

The experiment was conducted according to the procedure described in 6.4.9.1. The compound (5.17) (25 g, 33.7 mmol), Na<sub>2</sub>WO<sub>4</sub> (0.41 g, 1.24 mmol), Aliquat 336 (0.55 g, 1.24 mmol), H<sub>2</sub>O<sub>2</sub> (30% w/v) (35.5 g, 313 mmol). No precipitation was observed in the aqueous layer and the major compounds in the crude organic layer were identified as (5.11) and (5.17).

#### 6.4.9.4 Oxidative cleavage of 9,10-dimethoxy methyl oleate (5.18)

The experiment was conducted according to the procedure described in 6.4.9.1. The compound (5.18) (20 g, 55.9 mmol), Na<sub>2</sub>WO<sub>4</sub> (0.4 g, 1.2 mmol), Aliquat 336 (0.53 g, 1.2 mmol), H<sub>2</sub>O<sub>2</sub> (30% w/v) (32 g, 282 mmol). No precipitation was observed in the aqueous layer and the major compound in the crude organic layer was identified as (5.18).

#### 6.4.10 Oligomerization of oleic acid without catalyst

Oleic acid (5.5) (50 g, 177 mmol) and hydrogen peroxide (30% w/w, 100 g, 890 mmol) were weighed into a round bottom flask. The mixture was stirred and heated at 80 °C for 3 days. The mixture was poured into a separating funnel and CHCl<sub>3</sub> (50 ml) was added to it. The organic layer was separated from the aqueous layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and CHCl<sub>3</sub> was removed *in vacuo* to yield a colorless liquid (5.6) (50 g)  $\nu_{\max}/\text{cm}^{-1}$  3467 (OH) 2923, 2854 (C-H) 1708 (C=O) 1174 (C-O) 723 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 4.87-4.80 (2H, m, HCOC=O), 3.63-3.55 (2H, m, HCO) 3.45-3.38 (2H, m, HCO), 2.32 (6H, t, *J*=7.1 Hz, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.68-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.20 (72H, m,

CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 0.88 (12H, t, *J*= 6.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 179.2, 173.9 (C=O), 76.1 (HCOC=O), 74.4, 72.4 (HC-O), 33.9 (O=CCH<sub>2</sub>), 24.4 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 31.3, 29.5, 24.6, 22.8 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>); *m/z* (ES<sup>+</sup>) [M+Na<sup>+</sup>] (*n*=3) Required 935.7527, Found 935.7519

#### 6.4.11 General procedure for oligomerization of plant oil with succinic acid

##### 6.4.11.1 Oligomerization of soybean oil (5.24) with succinic acid as an example

Soybean oil (5.24) (5 g, 5.3 mmol), succinic acid (2.5 g, 21 mmol) and hydrogen peroxide (30% w/w, 30 g, 0.26 mol) were weighed into a round bottom flask. The mixture was stirred and heated at 80 °C for 7 days. The mixture was poured into a separating funnel and CHCl<sub>3</sub> (50 ml) was added to it. The organic layer was separated from the aqueous layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and CHCl<sub>3</sub> was removed *in vacuo* to yield a yellowish liquid (5.25) (6.5 g). *v*<sub>max</sub>/cm<sup>-1</sup> 3446 (OH) 2923, 2856 (C-H) 1736 (C=O) 1163 (C-O) 754 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 5.30-5.22 (1H, m, CHO), 4.31 (2H, dd, *J*= 11.9 Hz, 4.5 Hz, CH<sub>2</sub>O), 4.15 (2H, dd, *J*= 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.85-3.37 (4H, m, HCO), 2.63 (2H, t, *J*= 7.4 Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 2.33 (6H, t, *J*= 7.5 Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 1.66-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.52-1.20 (48H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.89 (9H, t, *J*= 7.5 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>): δ<sub>C</sub> = 177.9, 175.7, 173.2, 172.8 (C=O) 78.7, 76.9, 74.3, 72.3 (HC-O), 68.8 (HC-O), 62.1, 61.7 (H<sub>2</sub>C-O), 33.7, 28.3 (O=CCH<sub>2</sub>), 24.4 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.4, 22.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.7 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.4.11.2 Oligomerization of rapeseed oil (5.23) with succinic acid

The experiment was conducted according to the procedure described in 6.4.11.1. Rapeseed oil (**5.23**) (5 g, 5.3 mmol), succinic acid (2.7 g, 23 mmol) and hydrogen peroxide (30% w/w, 26 g, 0.23 mol), yellowish liquid (6.9 g);  $\nu_{\max}/\text{cm}^{-1}$  3450 (OH) 2924, 2854 (C-H) 1710 (C=O) 1164 (C-O) 755 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.30-5.22 (1H, m,  $\text{CH}\text{O}$ ), 5.12-5.04 (1H, m,  $\text{CH}\text{O}$ ), 4.90-4.78 (1H, m,  $\text{CH}\text{O}$ ), 4.29 (2H, dd,  $J$  = 11.8 Hz, 4.5 Hz,  $\text{CH}_2\text{O}$ ), 4.15 (2H, dd,  $J$  = 11.7 Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 3.80-3.30 (4H, m,  $\text{HCO}$ ), 2.66 (2H, t,  $J$  = 7.5 Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 2.33 (6H, t,  $J$  = 7.0 Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.70-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.54-1.20 (54H, m,  $\text{CH}_2\text{CH}_2$ ), 0.88 (9H, t,  $J$  = 6.8 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 178.6, 176.3, 173.3, 172.1 (C=O) 77.0, 74.4, 72.5 ( $\text{HC}-\text{O}$ ), 68.8 ( $\text{HC}-\text{O}$ ), 62.1, 61.9 ( $\text{H}_2\text{C}-\text{O}$ ), 33.9, 28.6 ( $\text{O}=\text{CCH}_2$ ), 24.6 ( $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 29.5, 25.1, 22.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.9 ( $\text{CH}_2\text{CH}_3$ )

#### 6.4.11.3 Oligomerization of palm oil (5.22) with succinic acid

The experiment was conducted according to the procedure described in 6.4.11.1. Palm oil (**5.22**) (5 g, 5.6 mmol), succinic acid (1.39 g, 11.7 mmol) and hydrogen peroxide (30% w/w, 13.4 g, 0.118 mol), a yellowish liquid (4.5 g);  $\nu_{\max}/\text{cm}^{-1}$  3451 (OH) 2925, 2856 (C-H) 1725 (C=O) 1125 (C-O) 744 ( $\text{CH}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 5.29-5.22 (1H, m,  $\text{CH}\text{O}$ ), 4.92-4.78 (2H, m,  $\text{CH}\text{O}$ ), 4.30 (2H, dd,  $J$  = 11.8 Hz, 4.6 Hz,  $\text{CH}_2\text{O}$ ), 4.13 (2H, dd,  $J$  = 11.9 Hz, 5.8 Hz,  $\text{CH}_2\text{O}$ ), 3.78-3.30 (4H, m,  $\text{HCO}$ ), 2.63 (2H, t,  $J$  = 7.5 Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 2.29 (6H, t,  $J$  = 7.5 Hz  $\text{O}=\text{CCH}_2\text{CH}_2$ ), 1.68-1.56 (6H, m,  $\text{O}=\text{CCH}_2\text{CH}_2\text{CH}_2$ ), 1.54-1.20 (64H, m,  $\text{CH}_2\text{CH}_2$ ), 0.87 (9H, t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 176.9, 173.6, 172.6 (C=O) 78.2,

76.6, 74.1, 72.1 ( $\text{HC-O}$ ), 68.6 ( $\text{HC-O}$ ), 61.8, 61.6 ( $\text{H}_2\text{C-O}$ ), 33.6, 28.9 ( $\text{O=CCH}_2$ ), 24.4 ( $\text{O=CCH}_2\text{CH}_2\text{CH}_2$ ), 29.4, 22.5 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{CH}_2\text{CH}_3$ )

#### 6.4.11.4 Oligomerization of cocoa butter (5.21) with succinic acid

The experiment was conducted according to the procedure described in 6.4.11.1. Cocoa butter (5.21) (5 g, 5.8 mmol), succinic acid (5.21) (0.70 g, 5.8 mmol) and hydrogen peroxide (30% w/w, 6.6 g, 58 mmol), a yellowish liquid (4.7 g) which was characterized by  $^1\text{H}$  NMR to be epoxidized cocoa butter.

#### 6.4.12 Oligomerization of soybean oil (5.24) with adipic acid

The experiment was conducted according to the procedure described in 6.4.11.1. Soybean oil (5.24) (5 g, 5.3 mmol), adipic acid (4 g, 28 mmol) and hydrogen peroxide (30% w/w, 32 g, 0.28 mol), a yellowish liquid (4.8 g) which was characterized by  $^1\text{H}$  NMR to be epoxidized soybean oil.

#### 6.4.13 General procedure for oligomerization of plant oil with phthalic anhydride

##### 6.4.13.1 Oligomerization of soybean oil (5.24) with phthalic anhydride as an example

Soybean oil (5.24) (5 g, 5.3 mmol), phthalic anhydride (4 g, 28 mmol) and hydrogen peroxide (30% w/w, 15 g, 0.138 mol) were weighed into a round bottom flask. The mixture was stirred and heated at 80 °C for 1 day. The mixture was poured into a separating funnel and  $\text{CHCl}_3$  (50 ml) was added to it. The organic layer was separated from the aqueous layer. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and  $\text{CHCl}_3$  was removed *in vacuo* to yield a yellowish liquid (5.29) (6.5 g).

$\nu_{\max}/\text{cm}^{-1}$  3449 (OH) 2924, 2854 (C-H) 1720 (C=O) 1599 (Ar-CH) 1069 (C-O) 743 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 7.90-7.60 (2H, m, Ar-H) 7.60-7.45 (2H, m, Ar-H), 5.32-5.22 (1H, m, CHO), 5.19-5.06 (1H, m, CHO) 4.29 (2H, dd,  $J$  = 11.9 Hz, 4.5 Hz, CH<sub>2</sub>O), 4.15 (2H, dd,  $J$  = 11.9 Hz, 5.9 Hz, CH<sub>2</sub>O), 3.90-3.35 (4H, m, HCO), 2.31 (6H, t,  $J$  = 7.5 Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 1.72-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.17 (48H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.87 (9H, t,  $J$  = 6.9 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 178.3, 173.3, 172.9 (C=O) 131.2, 129.2 (Ar-C) 83.1, 78.5, 74.4, 72.8 (HC-O), 68.7 (HC-O), 62.2, 61.9 (H<sub>2</sub>C-O), 33.8 (O=CCH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.5, 22.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.4.13.2 Oligomerization of palm oil (5.22) with phthalic anhydride

The experiment was conducted according to the procedure described in 6.4.13.1. Palm oil (5.22) (5 g, 5.6 mmol), phthalic anhydride (1.72 g, 21 mmol), hydrogen peroxide (30% w/w, 6.6 g, 58 mmol), a yellowish liquid (5.30) (6.7 g).  $\nu_{\max}/\text{cm}^{-1}$  3441 (OH) 2922, 2853 (C-H) 1738 (C=O) 1601 (Ar-CH) 1070 (C-O) 755 (CH<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 7.85-7.67 (2H, m, Ar-H) 7.58-7.47 (2H, m, Ar-H), 5.32-5.24 (1H, m, CHO), 5.17-5.04 (1H, m, CHO) 4.31 (2H, dd,  $J$  = 11.9 Hz, 4.6 Hz, CH<sub>2</sub>O), 4.15 (2H, dd,  $J$  = 11.9 Hz, 6.0 Hz, CH<sub>2</sub>O), 3.80-3.37 (4H, m, HCO), 2.31 (6H, t,  $J$  = 7.3 Hz O=CCH<sub>2</sub>CH<sub>2</sub>), 1.80-1.56 (6H, m, O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54-1.15 (64H, m, CH<sub>2</sub>CH<sub>2</sub>), 0.88 (9H, t,  $J$  = 6.4 Hz, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 177.9, 173.7, 172.7, 170.3 (C=O) 131.1, 129.1 (Ar-C) 78.4, 74.3, 72.5 (HC-O), 68.7 (HC-O), 62.0, 61.7 (H<sub>2</sub>C-O), 33.7 (O=CCH<sub>2</sub>), 24.5 (O=CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 29.4, 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 13.8 (CH<sub>2</sub>CH<sub>3</sub>)

#### 6.4.14 Polyurethane synthesized from estolides (5.6)

Estolides (**5.6**) (10 g, hydroxyl value = 230 mg KOH/g sample) was weighed into a round bottom flask and chloroform (50 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (7.7 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (**5.31**) was cured at 60 °C for 24 hours in an oven.  $\nu_{\text{max}}/\text{cm}^{-1}$  3337 (O=CNH) 2924, 2854 (C-H) 1727 (C=O) 1597 (aromatic =CH) 1095 (C-O) 721 (CH<sub>2</sub>)

#### 6.4.15 Polyurethane synthesized from oligomerized soybean oil with succinic acid (5.25)

Polyol (**5.25**) (10 g, hydroxyl value = 144 mg KOH/g sample) was weighed into a round bottom flask and chloroform (50 ml) was added to dissolve it. The round bottom flask was purged with dry nitrogen gas to remove any moisture from the system. Then, 4,4'-methylene diphenyl diisocyanate (MDI) (4.8 g) was added to the dissolved polyol. The NCO/OH ratio index was 1.02. The reaction mixture was heated to 60 °C under reflux condition for 24 hours. After 24 hours, some of the chloroform was removed by using a rotary evaporator and then polyurethane product was poured into a pre-heated mold at 60 °C. The polyurethane (**5.32**) was cured at 60 °C for 24 hours in an oven.  $\nu_{\text{max}}/\text{cm}^{-1}$  3337 (O=CNH) 2924, 2854 (C-H) 1727 (C=O) 1597 (aromatic =CH) 1046 (C-O) 723 (CH<sub>2</sub>)



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